Thermo-Chemical Treatment (TCT) of Polymers in Multi-Scale Reactors: A Kinetics and Life Cycle Assessment (LCA) Study

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I, *Sultan Majed Sultan Mohammed Al-Salem*, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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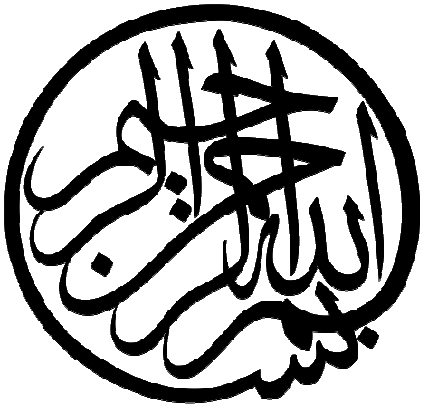

IN THE NAME OF GOD, THE MOST GRACIOUS AND MOST MERCIFUL

To my *Father's* soul, I wish he was here;

To my *Mother* whom always wondered where I was;

To my Family & Friends who believed in me;

To you all

[redacted]

'**WE** raise the degrees of whomsoever **WE** please, and ***above every one possessed of knowledge is the All-knowing one'***

Yusuf (Joseph) [12:76]

بسمك اللهم، ما شاء الله تبارك الرحمن بسمك اللهم، ما شاء الله تبارك الرحمن بسمك اللهم، ما شاء الله تبارك الرحمن

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ABSTRACT

The main reasons behind the success of the petrochemicals industry are not only the vast array of products that it provides - considered vital to our daily functions - but also the added value that it brings to the crude oil barrel price, making it a reliable venture for any concerned party. However, the industry is now faced with a fluctuating market and an unstable economy, which makes it imperative to find a more abundant and sustainable feedstock. Of all petrochemical derivatives, polymers (and their related industries) occupy the major share, and this makes the plastics industry a growing sector in terms of processing and conversion. Both virgin and waste plastics represent an attractive source of energy and product recovery.

The main objective of this work was to investigate the thermo-chemical treatment (TCT) of polymers at different scales, and the reactors studied ranged from micro laboratory scale to industrial units suitable for covering large market demands. Within this framework, the degressive behaviour of polyolefin polymers (three virgin grades and two recyclate ones) was investigated alongside the products yielded (gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), aromatics (single ring structures) and waxes (> C_{11}). This was achieved in a micro scale isothermal pyrolysis process, using 15 mg in a laboratory thermogravimetric analyser covering the temperature range of 500-600°C. The analysis led to the development of an n^{th} order novel model on the basis of lumped products yielded by pyrolysis. The degradation mechanism was used to develop the mathematical breakdown of the primary, secondary and tertiary reactions. The model developed predicts the yield of the four different products and the polymer residual fraction at any operating condition proving to be a useful tool for reactor design and simulation, where the production of a specific chemical at a certain operating condition is paramount.

In addition, laboratory scale isothermal pyrolysis experiments on end of life tyres (ELTs) were also conducted. This was achieved as a means to demonstrate the application of the concept previously applied to the polyolefins. A thermal cracking (degradation) scheme was proposed based on the global yielded products, which were lumped into four categories, namely gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char. The depolymerization kinetics (from primary, secondary and tertiary reactions) evaluation showed a high match with the experimental results obtained in this work.

Finally, a life cycle assessment (LCA) was conducted for three integrated scenarios that reflect the current (2012) treatment of waste plastics in the Greater London area. The scenarios studied utilised a fraction of the polymers treated as a feedstock for two industrial scale TCT technologies; namely a low-temperature pyrolysis reactor that works using BP® technology and a hydrocracking unit that utilises the Veba-Combi Cracking (VCC®) concept. The scenarios studied also include transfer stations, a dry materials recovery facility (MRF) and a combined heat and power (CHP) incineration unit. The energy recovered via the different processes studied, as well as the chemicals and petrochemicals recovered, were all considered as credits in the LCA conducted. Chemicals obtained by the TCT units are very valuable and can replace refinery cuts and petrochemicals (e.g. syncrude (crude oil), naphtha, heavy (waxes) fraction (comparable to atmospheric residue), gases (C_3 and C_4) refinery cuts, etc.). This led to a techno-economic analysis of the three integrated scenarios in order to assess the overall profitability. The analysis included capital, operating and maintenance costs, gate fees, transportation costs and corporation tax. The eligibility for governmental incentives (i.e. renewable obligation certificates (ROCs), levy exemption certificates (LECs) and packaging recovery notes (PRNs)) was also considered.

The results obtained from the work carried out and reported in this thesis point towards ideal strategies for the treatment of polymers within the urban environment. It also provides a detailed understanding of potential products from polymers introduced to TCT units. This also aids the optimum recovery of petrochemicals, chemicals and energy from different TCT processes, and could help the UK Government in meeting its energy policy targets. It can also contribute to the energy security through diversification of supply. Finally, it provides a perspective on the integration between the crude oil upstream industry and different petrochemical complexes and oil refineries, through the use of different TCT units to increase the production of petrochemicals in existing plants.

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I would like to start by thanking my primary supervisor, Dr. Paola Lettieri (ChemEng, UCL) for her support, encouragement and belief in me throughout my time in UCL. The opportunities that she presented me with were endless, and for that I thank you. Many thanks to my secondary supervisor, Dr. Lazaros Papageorgiou (ChemEng, UCL) who has guided me through the realm of GAMS and introduced me to its wonders.

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And the rest of the gang, *you know who you are*.

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Chapter 1

General Introduction

Polymers are the most versatile materials of our modern times. With certain plasticisers and additives (e.g. pigments, concentrates, anti-blockers, light transformers (LT), UV-stabilisers, etc.), they become what we know as plastics. Being a crude oil derivative, polymers present themselves as an advantageous option for a number of thermal treatments.

It is estimated that the production of plastics worldwide is growing at a rate of about 5% per year (APC, 2008) and this results in high estimates of almost 60% of plastic solid waste (PSW) being discarded in open space or being landfilled in many developing and developed countries (APM EU, 2008). Consequently, there is a desperate need for technologies that can recover products and energy, thereby solving the accumulated waste issue and tackling the increasing demand for energy worldwide.

This chapter highlights the motivation behind the study conducted and presented in this thesis and concludes with an outline of the contents of this thesis.

1.1. Introduction

Thermo-chemical treatment (TCT) is the processing and treatment of polymers in the presence of heat under controlled temperatures. TCT is capable of recovering energy, monomer fractions and valuable products such as gases (rich with low cut refinery products and hydrocarbons), tars (waxes and liquids very high in aromatic content) and char (carbon black and/or activated carbon), and such technologies include pyrolysis and hydrogenation.

Polymers are the basic building block of plastics, of which the UK consumed over 5 million tonnes in 2007 (WRAP, 2007), with 20,000 tonnes of plastics being sent to China on an annual basis for recycling, and a mere 7% being recycled in the UK (ImpEE, 2005). There are a

number of reasons which drive authorities in the UK to consider plastic recycling, recovery and treatment. The high consumption of plastics combined with the potential for extending existing local authorities collection systems are amongst these reasons.

Figure 1.1 illustrates the flow of plastics through the UK economy in the year 2000. The majority of the tonnage is within the consumed products sector and this leads to the disposal, treatment, recycling and energy from waste (EfW) technologies. Such technologies include (on an industrial scale) TCT processes (e.g. pyrolysis, hydrogenation, etc), incineration, and biological treatment, etc.

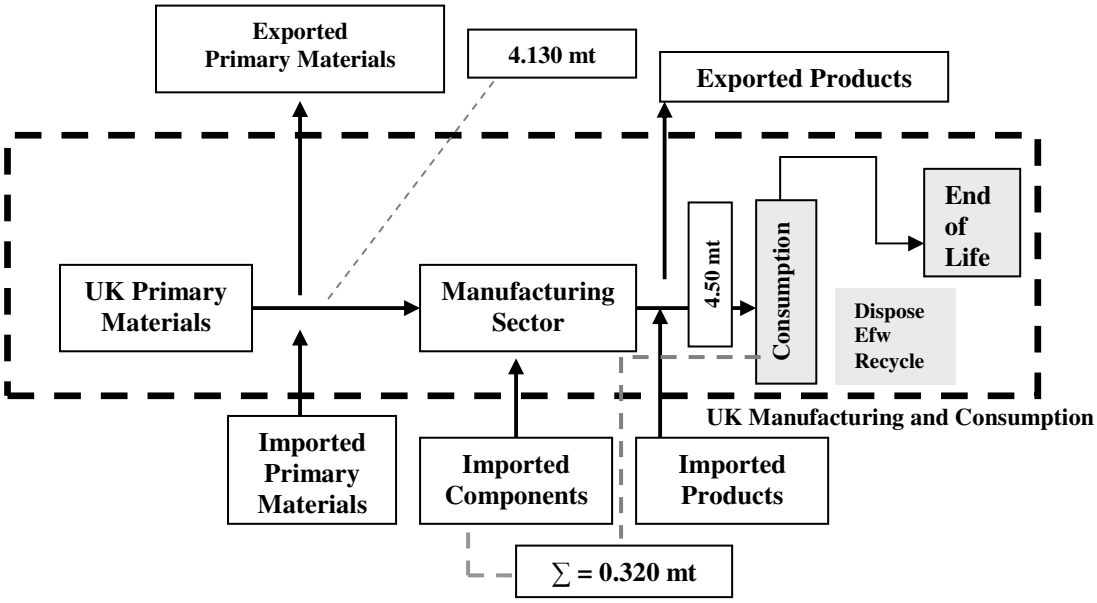

Figure 1.1 - Flow of plastic materials through the UK economy (2000).
Source: Smith, 2002; taken from Waste Watch final report (2003).
Abb. EfW - energy from waste.

Polymerisation technology still remains a success story and Europe is considered the major manufacturing region of plastics in the world. In 2007, the EU27+Norway and Switzerland produced 25% of the world's plastic production capacity; this amounted to 260 million tonnes (PEU, 2008), employing more than 1.6 million people, with a turnover in excess of 300 billion Euros. Yet still only a small percentage of waste (approximately 20.4%) is recycled and the most common option for disposal is by landfill or (co)-incineration (Westerhout et al., 1998a; PEU, 2008), both of which are associated with major environmental burdens. A valuable alternative process would be to convert and upgrade PSW by applying pyrolysis, whereby different operating conditions yield different products. The kinetics of the thermal pyrolysis defines the optimum conditions to maximise the yield of a desired product and this is required for the design of commercial pyrolysis reactors.

Figure 1.2 illustrates the flow of plastics from conversion to the end of life phase in the EU27 (with Switzerland and Norway) countries. The energy recovery rate remained stable at 29.2% reflecting how the sensitivity and planning complexity of this resource management technology has led to slow progress within society. In 2007, 12.4 million tonnes of plastics were landfilled, and despite a 3% per year growth over the past decade for post-consumer waste, the quantity going to landfill has remained stable (with recycling and recovery routes covering the tonnage obtained from the growth only).

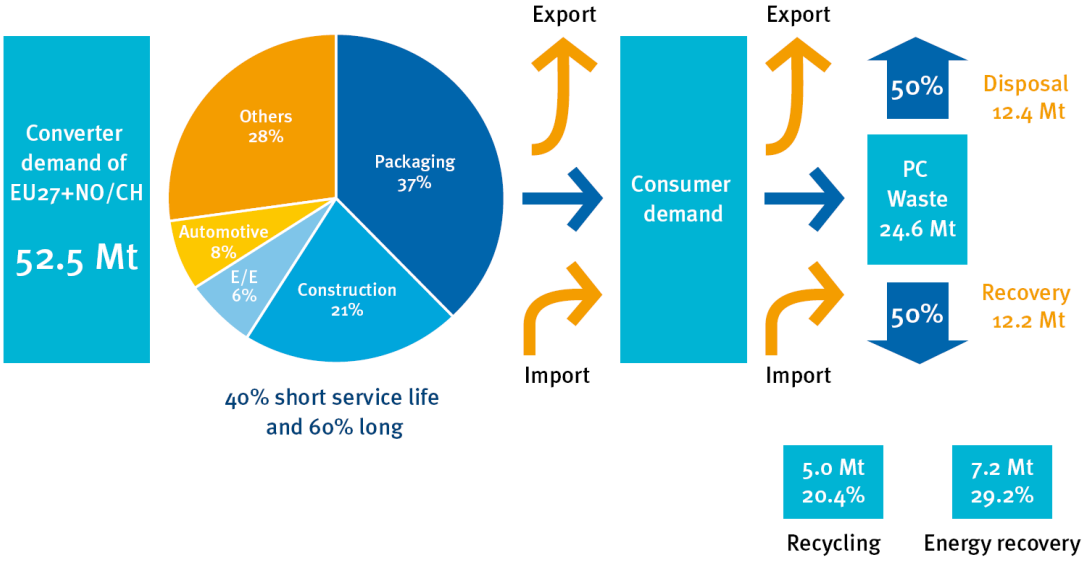

Figure 1.2 - Plastic materials from cradle to grave in the EU27+Switzerland and Norway.
Source: PEU, 2008.
Abb. PC - petrochemical.

However, there remains a lack of understanding regarding the behaviour of polymers undergoing TCT (namely pyrolysis). A comprehensive model that accounts for all products and which can be applied by the concerned industry describing the degressive mechanism of the polymer tested, would be highly desirable. Another gap within the current research is the assessment of environmental burdens associated with TCT units, especially in the case of Greater London. Furthermore, techno-economic studies of TCT are scant and research and development (R&D) activities reports are not sufficiently transparent to show the recent status of the depolymerisation industry.

1.2. Research Goals and Objectives

The interest in thermo-chemical treatment (TCT) processes began in the 1950s, when the application of laboratory scale TCT with different media (such as the inert gases: N_2, Ar, He, and partial oxygen) was focused on the elemental analysis it provided for the treated material. Soon after, different materials were used as feeds and interest in kinetics, design and implementing these processes on an industrial scale began to grow.

The industrial implementation of TCT units led to the recognition of the advantages it could provide. These include the production of valuable chemicals, petrochemicals and energy from the treatment of different materials, as well as the possibility of reducing the overall costs in crude oil complexes when TCT units are integrated within a processing scheme. Polymers are crude oil derived materials; hence they embody energy and a high calorific value that could be utilised as a feedstock rather than occupying a large proportion of municipal solid waste (MSW) and other solid waste streams and/or being discarded in open space. Thermo-chemically treated plastics can produce a number of valuable petrochemicals, including benzene-toluene-xylenes (BTX), ethene, propene, butadiene and styrene, which are considered essential in any petrochemical chain.

The treatment of polymers in the form of commercial grade plastics at different scales is the main theme of this work. This study may benefit both the crude oil industry and the solid waste management sector. A detailed understanding of thermo-chemical processes, the behaviour of materials subjected to TCT, the energy generated and products formed, may inform interested parties with different industrial infrastructure developmental options. In addition, there are possibilities for integration with other related industries, e.g. oil refineries, chemical and petrochemical complexes, etc.

The main goal of this research is to study the TCT of polymers in a number of venues and on different scales. The main objectives are as follows:

a. To investigate the behaviour of polymers at micro scale under thermal cracking conditions in inert atmospheres. N_2 was chosen as a medium for thermolysis (i.e. the pyrolysis process) of the polymers studied. Three virgin polymers and two recyclate grades were subjected to isothermal pyrolysis in a thermogravimetric analyser (TGA), i.e. fixed bed laboratory reactor. The products yielded were identified and lumped into four categories: Gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}) and waxes (> C_{11}). The polymers degressive behaviour was studied and differences between the grades treated are also reported.

b. To develop a novel model based on lumped product analysis (e.g. gases, liquids, aromatics, etc.) that accounts for the polymer fraction (residual) and the other formed products. Numerous attempts have been undertaken to develop a thermal degradation scheme, usually via a simple approach of parallel reactions from polymer to products (McCaffrey et al., 1995; 1998; Williams and Williams, 1997; 1999a; 1999b; Horvat and Ng, 1999). Yet differences are always present due to variations in polymer's characteristics (e.g. molecular weight, presence of weak links, additives, etc.) and differences in experimental conditions from which kinetic data are calculated

(McCaffrey et al., 1995). In this work, a model of the n^{th} order is proposed based on the experiments conducted. The model determines the amount of liquids, gases, waxes and aromatics produced by weight (%). This ultimately will provide a better understanding of the TCT of the polymeric material and aid in the intensification of the process (in terms of product yields). The isothermal mode of operation was chosen and the model proposed was validated against experimental results. The mathematical model of the mechanism proposed was based on mass balances and kinetic rate equation analysis. The derivation of the model was based on mass fractions.

c. To develop a thermal degradation mechanism using a similar approach as applied for the polyolefin materials based on laboratory scale isothermal pyrolysis experiments on end of life tyres (ELTs). The model was based upon the global yielded products, which were lumped into four categories, namely gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char.

d. To perform a life cycle assessment (LCA) on different integrated scenarios (incorporating TCT units in the Greater London area, GLA) with the aim of evaluating the environmental burdens associated with the different stages of each scenario. The type of study performed was an attributional life cycle assessment (ALCA), which is concerned with describing the environmental relevant physical flows to/from a life cycle and its sub-systems (Eriksson et al., 2007). The environmental impacts avoided by the displaced energy and products recovered were included. The scenarios studied included transfer stations (TS), treatment of dry recyclables in a materials recovery facility (MRF, located in the Borough of Greenwich, London) and an incineration unit (IU, located in the Borough of Lewisham, London). Boroughs of the Greater London area and a city in Devon (namely Exeter) were chosen as points of waste origin. These boroughs were chosen due to the fact that current reports and industrial data show that the City of Exeter sends dry waste to the Greenwich MRF in London.

e. To conduct a techno-economic analysis on the integrated scenarios, in order to assess the most profitable option for the GLA. Chemicals obtained by the TCT units are very valuable and can replace refinery cuts and petrochemicals (e.g. syncrude (crude oil), naphtha, heavy (waxes) fraction (comparable to atmospheric residue), gases (C_3 and C_4) refinery cuts, etc.). The techno-economic analysis included capital and operating and maintenance costs, gate fees, transportation costs and corporation tax (CT). The eligibility for governmental incentives (i.e. renewable obligation certificates (ROCs), levy exemption certificates (LECs) and packaging recovery notes (PRNs)) was also considered.

1.3. PhD Thesis Outline

The thesis is divided into seven chapters. This introductory chapter addresses the main issues concerning polymerisation/depolymerisation, the benefits of TCT technologies and the overall work objectives. In Chapter 2, a review of the previously published literature relating to the subject matter is given. Research on both modes of pyrolysis (isothermal and dynamic) is presented and the main findings are illustrated. In addition, details of industrial technologies are described, with an emphasis on pyrolysis schemes. In Chapter 3, the effects of micro-scale pyrolysis (using TGA in isothermal mode) are studied to assess the behaviour of five different polyolefins in inert atmosphere pyrolysis. Chapter 4 presents the results of applying a similar lumped product model to isothermal results obtained from ELTs. In Chapter 5, a detailed review is given on LCA methodology and application. In Chapter 6, an attributional LCA is performed around the GLA, and the burdens associated with the scenarios developed are assessed. In addition, the integration of TCT industrial units with a MRF and an IU are discussed. The seventh and final chapter draws a number of conclusions from the work carried out, together with a number of recommendations for future work.

Chapter 2

Literature Survey: Thermo-Chemical Treatment Processes

In this chapter chemical (tertiary) treatment of polymers, including advanced thermo-chemical treatment (TCT) processes in inert atmospheres (i.e. pyrolysis) is reviewed. A special emphasis is given to reactor design aspects, thermal cracking kinetics and conditioning effects on product yields. Descriptions of different TCT processes, their benefits and current research activities are also detailed. Other processes and treatment methods (e.g. hydrolysis, hydrocracking, gasification, degradative extrusion, etc.) are also discussed to provide a detailed view of polymers thermo-chemical and chemical treatments. Experimental and kinetics modelling work in this thesis focuses on the pyrolysis of polymers and end of life tyres (ELTs, see Chapters 3 and 4); therefore, weight loss (degressive) kinetics and degradation mechanisms modelling are discussed in depth.

Parts of this chapter were published in:

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**). Recycling and recovery routes of plastic solid waste (PSW): A review, *Waste Management*, **29(10)**; 2625-2643.

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**). The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, *Progress in Energy & Combustion Science*, **36(1)**; 103-129.

2.1. Polymers and Polymerisation Technology

Polymers have solely replaced classical materials in many sectors, specifically wood and metals. Polymers (and polymer composites) also contribute to our daily functions in many aspects and applications, from packaging, automobiles, clothing, appliances and electrical and vehicle equipment, to insulations, industrial applications, greenhouses, automotive parts, aerospace and mulches. Plastics (virgin or waste) are composed of polymers and additives, and

understanding polymers, in terms of their structure and origin is paramount for the assessment and comprehension of their behaviour under thermal treatment conditions. Monomers are small, single molecules (e.g. hydrocarbons, amino acids, etc.) that bond together to form a polymer through a process called polymerisation.

In a polymer, the structure (linear, branched or networked) and backbone is composed of a number of repeating units[1] (McCrum et al., 1997). Due to the fact that polymers are vast (in type, behaviour, structure and synthesis mode), a number of classification systems have been developed and used over time. Today, the most common classification used is based upon a polymer's response to heating, whereby polymers are classified as either thermoplastics or thermosets (Figure 2.1). Thermoplastics soften when heated and harden again once cooled. This is the most common type of polymer and encompasses almost all types of plastics and polyolefins.[2] Due to these characteristics, thermoplastics make an ideal material for recycling purposes under thermo-chemical, thermal, and thermo-mechanical set-ups. Typical polymers of this sort are polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET).

Polymerisation processes cover the majority of the petrochemicals industry worldwide. The main step in general and in polyolefin upgrading in particular, is the conversion process of the raw gas (e.g. ethylene, propylene, etc.) from naphtha or natural gas cracking to the desired polymer product (e.g. PE, PP, etc.). This process is by far the most important in the production cycle (under a pressure range of 100-300 psi and a temperature over 100°C), and is commonly achieved by means of catalytic conversion in fluidised bed reactors (FBR). Currently, BP® produces more than 150 commercial grades of polymers (mostly PE), mainly at Wilton (England), Grangemouth (Scotland), and Asian ventures in Indonesia, Malaysia and the Philippines.

[1] The repeating unit in a polymer chain is often referred to as the *mer*. Hence, a monomer is a single *mer* unit (n=1) and a repetition in the units along a chain is referred to as a polymer ($n \geq 103$).

[2] A *polyolefin* (PO) is a polymer produced from a simple olefin (alkene C_nH_{2n}) as a monomer. Examples of such include PE and PP which results from the original monomers of ethylene (ethene) and propylene (propene), respectively.

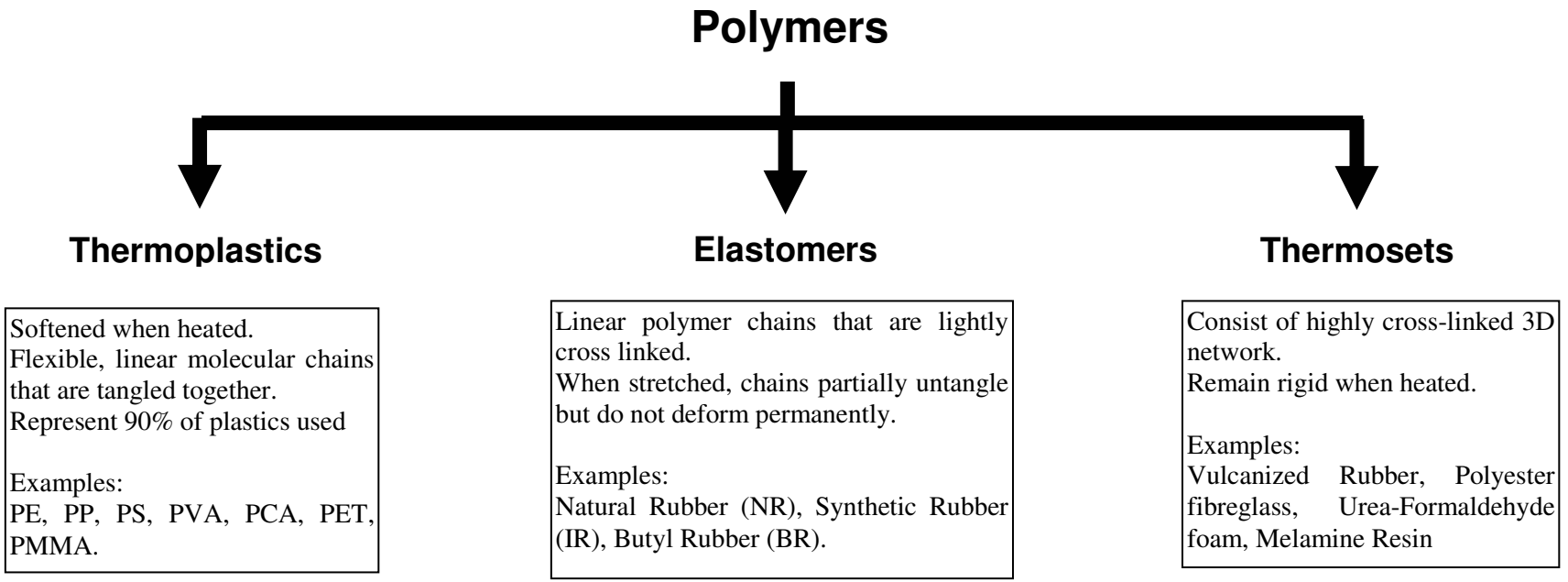

Figure 2.1 - Polymers classification (according to their physical properties) with respect to their behaviour and response to/after heating.
Source: McCrum et al., 1997.
Note: This is the most recent classification and currently is the most used one.

2.2. Plastic Solid Waste: Quantities, Generation and Trends

Plastics as waste articles, are found in all major municipal solid waste (MSW) categories and plastic solid waste (PSW) is found to be comprised mainly of containers and packaging plastics (i.e. bags, sacks, and wraps; soft drink, milk, and water containers). These items represent the highest percentage in the final assessed stream of MSW (USEPA, 2002; 2008).

In the UK, studies show that PSW constitutes 7% of the final waste stream (Parfitt, 2002), whereas in the US, PSW found in MSW has increased from 11% in 2002 (USEPA, 2002) to 12.1% in 2007 (USEPA, 2008). Years of research, study and testing have resulted in a number of treatment, recycling and recovery methods for PSW that can be economically and environmentally viable (Howard, 2002). The plastics industry has successfully identified workable technologies for recovering, treating, and recycling of waste from discarded products. In 2002, 388,000 tonnes of PE were used to produce various components of textiles, of which 378,000 tonnes were made from PE discarded articles (Gobi, 2002).

The growth of post-consumer plastic waste is the result of several reasons, namely:

a. Plastics continue to substitute alternative materials (e.g. wood, metal … etc.).

b. Economic growth drives greater consumption.

c. Smaller households require more packaging per person, thus more ready-made single-portion meals, carrier bags, etc. are consumed.

The plastics industry is committed to meeting the current needs of today without compromising the needs of tomorrow. In the UK, 95% of PSW arising from process scrap (≈ 250,000 tonnes) was recycled in 2007 (EA, 2001). PSW from commercial grade resins have been successfully recycled from a number of end products, including: automobile parts, appliances, textiles, mulches, greenhouses and films. Polymerisation and plastic conversion has taken its toll on every economy, and it is estimated that the plastic sector accounts for 7.5% of the UK's demand for chemicals annually (Waste Watch, 2003). However, more investment in monomers, valuable chemicals and energy recovery facilities is needed to divert streams which cannot be eco-efficiently recycled from landfill. An analysis of plastic materials consumption on a per capita basis shows a growth to approximately 100 kg in the North America Free Trade Agreement (NAFTA) countries and Western Europe (WE), with the potential to grow towards 140 kg per capita by 2015. The highest potential for growth can be found in the rapidly developing parts of Asia, where currently the consumption per capita is only around 20 kg.

In a European context, it is the new member states which are expected to see the biggest percentage increase as their economies develop. The current average per capita consumption in these countries is between 50 and 55 kg, a little more than half of that of the old member states (PEU, 2008).

The material recycling and energy recovery of post-consumer plastics waste varies significantly in different countries. In some countries like Switzerland, Germany and Denmark, there is very little landfill and these countries are very close to completing their diversion-from-landfill strategy. The progress of this strategy is slow on average, with recycling (mechanical and chemical) across the EU27+Norway and Switzerland increasing from 19.5% in 2006 to 20.4% in 2007, while energy recovery remained stable at 29.2%. Strong efforts will be required in many member states to capture the full potential offered by a diversion from landfill strategy, namely greenhouse gasses (GHGs) emission savings, enhanced resource efficiency, energy security and the avoiding of landfill penalties.

In summary, the production of polymers and plastics conversion covers the majority of the petrochemicals and petrochemical derivatives industry and markets. This is reflected in MSW, in which PSW constitutes 7% of the final stream in the UK (Parfitt, 2002). The versatility and light weight of plastics (compared to wood, metals, etc.) are amongst the main reasons for the growth of post-consumer plastics. In NAFTA and WE countries, a potential growth to 140 kg per capita is anticipated by the year 2015 (PEU, 2008). These estimates show an urgent need for the recovery of chemicals, petrochemicals and energy from articles discarded or considered as scrap.

2.2.1. Re-Use and Major Sorting Techniques

Re-using plastics is always noted as a preferable choice to recycling; it uses less energy and fewer resources, conserves fossil fuels since plastic production uses 4-8% of global oil production, i.e. 4% as feedstock and 4% during conversion (Perdon, 2004; JCR, 2006) and reduces carbon-dioxide (CO_2), nitrogen-oxides (NO_x) and sulphur-dioxide (SO_2) emissions. Sorting of plastics is an essential step within recycling (MOEA, 2001; EPIC, 2003).

In the case of rigid plastics, heavy medium separation is usually applied (Kang and Schoenung, 2005). This is achieved by adding a modifier to water or by using tetrabromoethane (TBE); however, this process is considered costly and can lead to contamination of the recovered plastics (Veit, 2002; Kang and Schoenung, 2005). Density sorting methods are not particularly helpful in PSW sorting because most plastics are very similar in density. To enhance the effectiveness of density separation, hydrocyclones (utilising centrifugal forces) are commonly used to enhance the material wettability (APC, 1999). Another major technique

employed in PSW sorting is triboelectric separation. Materials with a size between 2-4 mm are settled in a rotating drum to allow charging and sorting (Xiao, 1999).

Since plastics are present in commercial and industrial waste (DEFRA, 2009), the recovery routes are of essential importance in the selection of the proper treatment method. Waste is typically discharged in depots which allow collection vehicles to avoid travelling uneconomic distances. These depots are typically referred to as transfer stations (TSs, Last, 2008a). When these TSs incorporate sophisticated methods for treatment and sorting, they are called material recovery facilities (MRFs) (Last, 2008b). Components of mixed waste (recyclables) are extracted through the use of mechanical means, and depending on the sophistication of the plant, organics can also be recovered (dirty MRFs).

MRFs employ a system of conveyers which carry the recyclables over sorting screens. Nevertheless, a significant amount of hand-sorting of materials is typically employed in the process. A steady increase in clean (dry) MRFs has been reported in the UK, which is due to the introduction of separate recycling collections and an increase in recycling tonnage (Last, 2008b). In contrast, dirty MRFs have had limited success in the UK due to the volatility of the recycling market (Last, 2008b).

2.3. Routes of Treatment and Recovery: Back to Petrochemicals via Depolymerization

Value from PSW should be recovered through either recycling or energy and fuel recovery. Residual waste from different recycling processes (i.e. refuse-derived fuel, RDF) should be treated separately, either by thermo-chemical means or by incineration, and energy that is then recovered as heat or electricity, can be used for power generation. PSW recycling processes can be allocated into four major categories (Mastellone, 1999): re-extrusion (primary), mechanical (secondary), chemical (tertiary) and energy recovery (quaternary). Each method provides a unique set of advantages that makes it particularly beneficial for logistical requirements, applications or requirements. Primary treatment involves the introduction of plastic scrap into the heating system of a plant, and may be referred to as in-house recycling. Mechanical recycling (i.e. secondary or material recycling) involves physical treatment. Chemical recycling (encompassing feedstock recycling) produces feedstock chemicals for the chemical industry, and energy recovery involves complete or partial oxidation of the material, producing heat, power and/or gaseous fuels, oils and chars in addition to by-products that must be disposed of, e.g. ash.

The continued development of recycling and recovery technologies, investment in infrastructure, the establishment of viable markets and participation by industry, government and consumers, are all considered priorities of the highest order (Scheirs, 1998). In all recycling processes (plastic, metal, paper recycling, etc.), technical and economic feasibility and overall commercial viability of advanced recycling methods must be considered in each step of the recycling chain (Frisch, 1999). This in contrast makes it an absolute to maximise profits from structure design of any thermal treatments. Collection, processing, and marketing are each crucial to the success of chemical recycling and energy recovery. Today, with few exceptions, these technologies remain developmental and have not yet been proven to be sustainable in a competitive market. Nevertheless, they remain of considerable interest for their longer term potential.

2.3.1. Chemical Treatment

Chemical (tertiary) treatment is a term used to refer to advanced technology processes which convert plastic materials into smaller molecules, usually liquids or gases, which are suitable for use as a feedstock for the production of new petrochemicals and plastics (Mastellone, 1999). Almost no argument exists that states that the best utilisation of PSW is via tertiary treatments, i.e. chemical recycling, due to their high calorific value (Table 2.1).

Table 2.1 Calorific Value of Major Polymers in Comparison to Common Fuels.
Source: Williams and Williams, 1997; Mastellone, 1999.

Item	Calorific value (MJ kg^{-1})	Item	Calorific value (MJ kg^{-1})
Polyethylene	43.3-46.5	Gas Oil	45.20
Polypropylene	46.50	Heavy Oil	42.50
Polystyrene	41.90	Petroleum	42.30
Kerosene	46.50	Household PSW mixture	31.80

The term chemical is used to indicate that the chemical structure of the polymer will be altered. Products of chemical recycling have proved to be useful as fuel, and the technology behind its success is the *depolymerisation* processes that can result in a very profitable and sustainable industrial scheme, providing a high product yield and minimal waste. Under the category of chemical recycling are advanced processes (similar to those employed in the petrochemical industry), such as pyrolysis, gasification, liquid-gas hydrogenation, viscosity breaking, steam or catalytic cracking and the use of PSW as a reducing agent in blast furnaces. Recently, much attention has been paid to chemical recycling (mainly non-catalytic thermal cracking (thermolysis), catalytic and steam cracking) as a method of producing various fuel fractions from PSW (Aherenfeldt, 2007; Robinson, 2009; Economopoulos, 2010; Buttler et al., 2011; Blengini et al., 2012).

By their nature, a number of polymers are advantageous for such treatment; PET and certain polyamides (nylon 6 (PA 6) and nylon 66) can be efficiently depolymerised. In particular, PE has been targeted as a potential feedstock for fuel (gasoline) producing technologies, and there is also a growing interest in developing value added products such as synthetic lubricants via PE thermal degradation (McCaffrey et al., 1995).

Ever since the first synthetic polymer was produced in the 1940s, PSW has been increasing, with recycling and recovery routes being researched globally (Horvat and Ng, 1999). Therefore, the production cycle of polymers must cover the integrated waste management system (IWMS) in every cradle to grave loop, as illustrated in Figure 2.2.

The development of value added recycling technologies is highly desirable as it would increase the economic incentive to recycle polymers (Horvat, 1996). Several methods for chemical recycling are presently in use, such as direct chemical treatment involving gasification, smelting by blast furnace (Asanuma and Ariyama, 2004) or coke oven (Kato et al., 2004), and degradation by liquefaction (Steiner et al., 2002). Condensation polymers such as PET and nylon undergo degradation to produce monomer units, i.e. feedstock/monomer recycling (Yoshioka et al., 2004), while vinyl polymers such as polyolefins produce a mixture containing numerous components for use as a fuel. Various degradation methods for obtaining petrochemicals are presently under investigation, and conditions suitable for pyrolysis and gasification are being extensively researched (Aguado et al., 2007; Buttler et al., 2011). Catalytic cracking and reforming facilitates the selective degradation of waste plastics, and solid catalysts such as silica-alumina, ZSM-5, zeolites, and mesoporous materials are common for these purposes. These materials effectively convert polyolefins into liquid fuel, resulting in lighter fractions compared to thermal cracking. The main advantage of chemical recycling is the possibility of treating heterogeneous and contaminated polymers with limited pre-treatment. If a recycler is considering a recycling scheme with a target of 40% or more, it should deal with materials that are very expensive to separate and treat; thus, chemical recycling becomes a viable solution (Scheirs, 1998). Petrochemical plants are much greater in size (6-10 times) than plastic manufacturing plants. Therefore it is essential to utilise petrochemical plants and supplement their usual feedstock by using PSW derived feedstock.

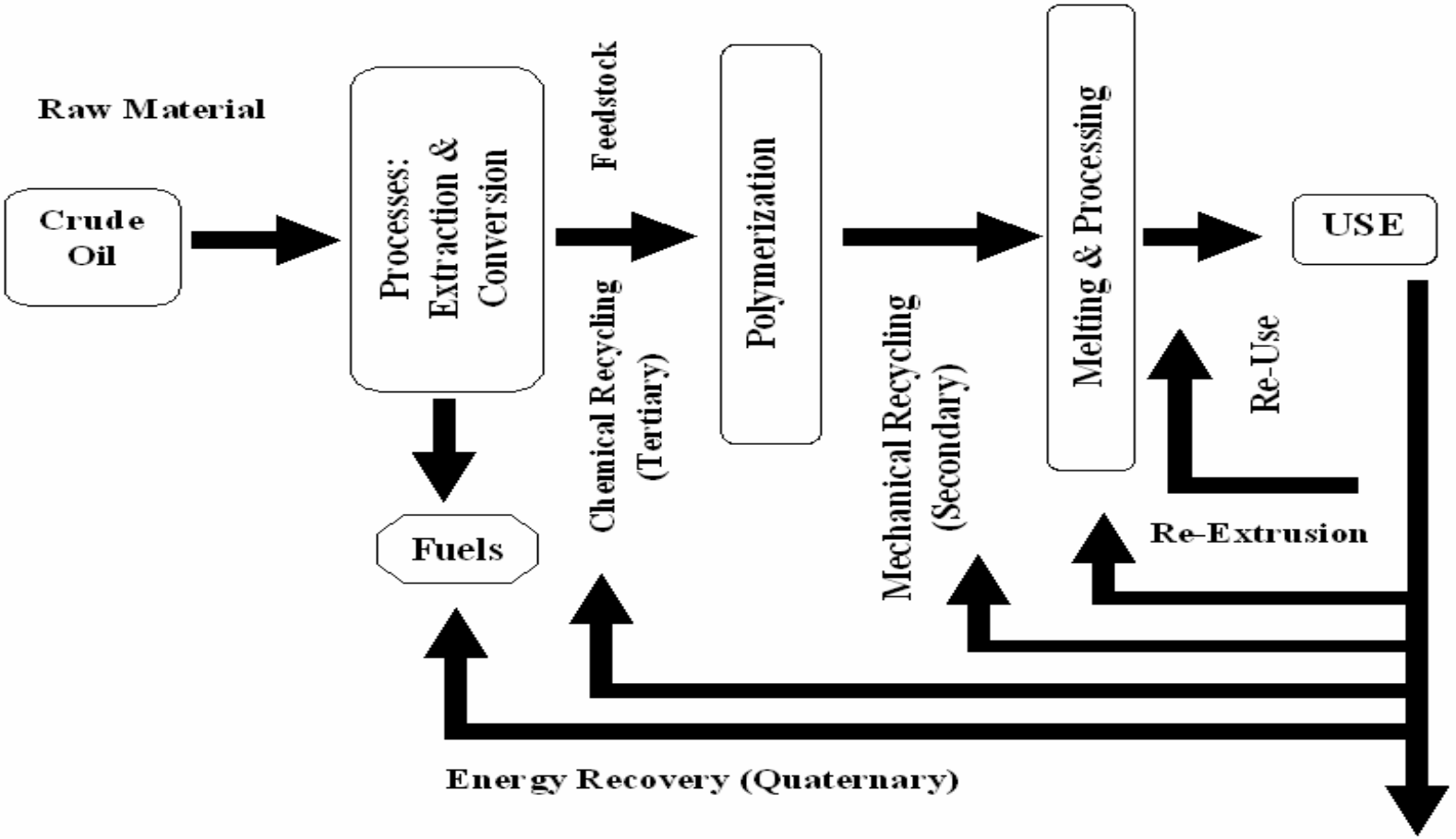

Figure 2.2 - Treatment methods related to the production cycle of polymers.
Source: Mastellone, 1999.

In summary, recycling and treatment of PSW can be allocated to four main categories (Mastellone, 1999), in which an ascending hierarchy has been established as follows:

i. Re-extrusion of polymers (primary treatment): in which the process scrap is re-introduced into the production cycle. According to the UK Environmental Agency (EA, 2001), 250 ktonnes of plastic were recycled in this manner in 2001.

ii. Mechanical (secondary) treatment: where plastics are subjected to physical treatment. This typically involves blending and extrusion processes.

iii. Chemical (tertiary) treatment of polymers: this group of technologies alter the chemical structure of the polymer, resulting in a number of chemicals. Treating heterogeneous and contaminated polymers with limited pre-treatment is one of the main advantages this method provides. When heat is used in controlled temperatures (with or without catalysts) this category is referred to as TCT.

iv. Energy recovery (quaternary treatment): this method involves complete or partial oxidation of the material, producing heat, power and/or gaseous fuels, oils, chars and ash.

Valuable petrochemicals and energy can be recovered from various types of chemical treatments of polymers. Advantages of chemical treatment methods include the treatment of mixed and contaminated plastics with minimal pre-treatment, the production of valuable petrochemicals and the recovery of energy in the form of heat and electricity. Since most chemical treatment technologies are applied by crude oil processing production lines (e.g. pyrolysis, steam-cracking, hydrocracking), integration with refineries and petrochemicals complexes is an attractive option for major oil companies. It is essential to utilise petrochemical plants by supplementing their usual feedstock with PSW derived feedstock. In addition, the recovery of desirable chemicals and energy makes chemical means of treatment a very advantageous treatment method that warrants further research and development (R&D).

2.3.2. Thermolysis: Definition and Schemes

Thermolysis is the treatment of PSW in the presence of heat under controlled temperatures without catalysts, and it is a TCT method. Advanced TCTs of PSW in the presence of heat under controlled temperatures provide a viable and an optimum engineering solution for energy and product recovery. Not only has this method recovered healthy monomer fractions, reported as up to 60% (Smolders and Baeyens, 2004), but it also produces valuable products that can be summarised as gases (rich with low cut refinery products and hydrocarbons), tars (waxes and liquids very high in aromatic content) and char (carbon black and/or activated carbon).

Thermolysis processes can be divided into advanced thermo-chemical processes or pyrolysis (thermal cracking in an inert atmosphere), gasification (in the sub-stoichiometric presence of air, usually leading to CO and CO_2 production) and hydrogenation (hydrocracking) (Ahrenfeldt, 2007). Figure 2.3 shows different thermolysis schemes, the main technologies and the main products obtained, as described by Mastellone (1999).

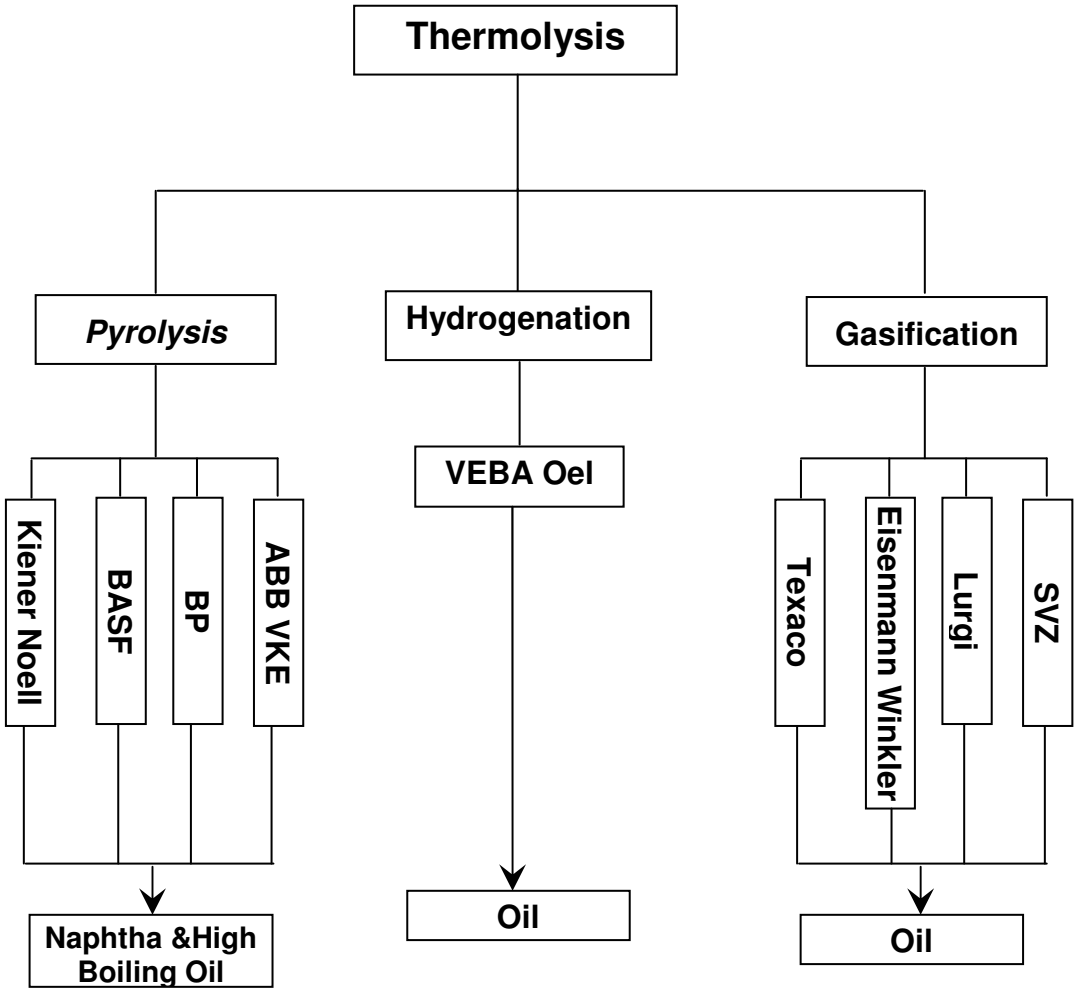

Figure 2.3 - Different thermolysis schemes with reference to the main technologies.
Source: Mastellone, 1999.

2.3.3. Advantages of Pyrolysis and Benefits to the Petrochemicals Industry and Production Cycle

The development and expansion of the petrochemical industry in recent years has been characterised by a concentration of production and an increase in the size of individual process units and process sections. Along with the use of larger process units has come an improvement in the production economics and this has led to more favourable conditions for the combined utilisation of raw material resources (including by-products and wastes).

Concurrently, the concentration of petrochemical production has led to problems in raw material supplies. Only the largest petroleum refineries can serve as a stable source of feedstock. However, the lack of any such refineries in many districts has created a need for establishing an autonomous raw material base equipped with specialised production units or refineries for primary crude oil processing with the specific purpose of producing petrochemical feedstock. It is difficult to produce large amounts of naphtha from pyrolysis (cracking) within the ranks of the existing fuel profile refineries. Consequently, there is a need to develop more industrial TCT units.

Integrating upstream, downstream and end-of-stream (petrochemicals) processing in many production cycles will evidently aid in the supply chain and demand coverage. This is the new trend currently studied in low feedstock cost countries (e.g. the State of Kuwait), and will ultimately reduce the cost of shared utilities and lower transportation cost (AOG, 2009). Many products from TCT (in general) and pyrolysis (in particular) can serve the industry as a number of refinery cut replacements. Figure 2.4 shows the major TCT products obtained from different feedstock recycling processes, and Table 2.2 summarises some of the petrochemicals that can be produced via pyrolysis. Other benefits of integrating pyrolysis units with existing refineries include: (i) high H/C ratios of polyolefins compared to heavy residues, hence the production of more valuable products upon thermal decomposition; (ii) synergistic effects can be observed upon processing of polyolefins with crude oil derivatives that produces better quality products (Butler et al., 2011). The possibilities for integration with existing oil refineries infrastructure are illustrated in Figure 2.5.

Pyrolysis provides a number of other advantages, such as (i) operational advantages, (ii) environmental advantages and (iii) financial benefits. Operational advantages could be described through the utilisation of residual output of char being used as a fuel or a feedstock for other petrochemical processes. An additional operational benefit is that pyrolysis requires no flue gas clean up, as the flue gas produced is mostly treated prior to utilisation. Environmentally, pyrolysis provides an alternative solution to landfilling and reduces GHGs and CO_2 emissions. Financially, pyrolysis produces a high calorific value fuel that could be

easily marketed and used in gas engines to produce electricity and heat. Several obstacles and disadvantages do exist for pyrolysis, mainly in the handling of the char produced (Ciliz, 2004) and the treatment of the final fuel produced, if specific products are desired. In addition, there is insufficient understanding of the underlying reaction pathways, which has prevented a quantitative prediction of the full product distribution. Recycling pyrolysis products back into the production cycle is the ultimate goal for petrochemical industries. Williams and Williams (1999b) describe the experiences of a UK consortium of companies regarding such potential petrochemical products, and these are discussed later in this thesis (see Chapters 5 & 6).

Table 2.2 Summary of main petrochemicals (PCs) produced via pyrolysis of POs.
Source: Butler et al. (2011)

Product	Price (€/tonne)	Process	Feedstock	Intermediate/final product
Ethene	692-1,084	Thermal cracking	Ethane, propane, naphtha, gas oil	PE manufacture (>50 wt%), antifreeze, polyester fibres, PVC, PS plastic & foam, soaps, plastics, detergents
Propene	692-1,279	Thermal cracking	Ethane, propane, naphtha, gas oil	PP, plastics, fibres, foams, cumene (IP), C_4 alcohols, oligemers, soaps, detergents
Butadiene	602-1,656	Thermal cracking Dehydration	Ethane, propane, naphtha, gas oil, butane/butenes	SBR (tyres), elastomers, nylon monomers
Benzene	710-922	Catalytic reforming/hydrodealkylation	Naphtha, toluene	Styrene, cumene, cyclohexane, polyurethanes
Toluene	582-828	Catalytic reforming	Naphtha	Gasoline octane enhancer, benzene, TNT (explosive)
Xylenes	597-862	Catalytic reforming	Naphtha	Gasoline, benzene, solvents, PET, textiles fibres, photographic film, bottles, plasticizers, unsaturated polyester resins, alkylated resins

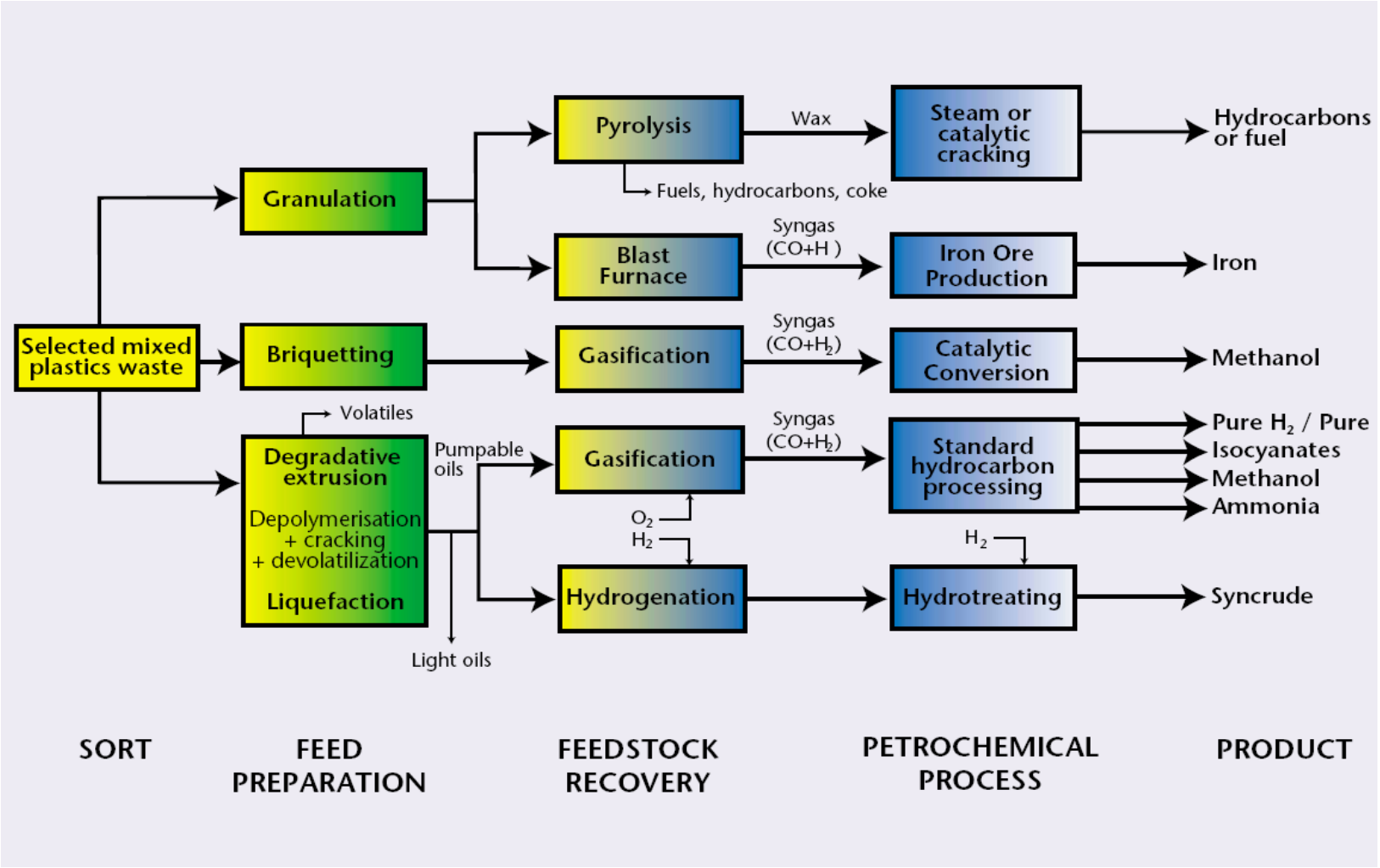

Figure 2.4 - Possible chemical products obtained from TCT. Source: ISOPA, 2001.

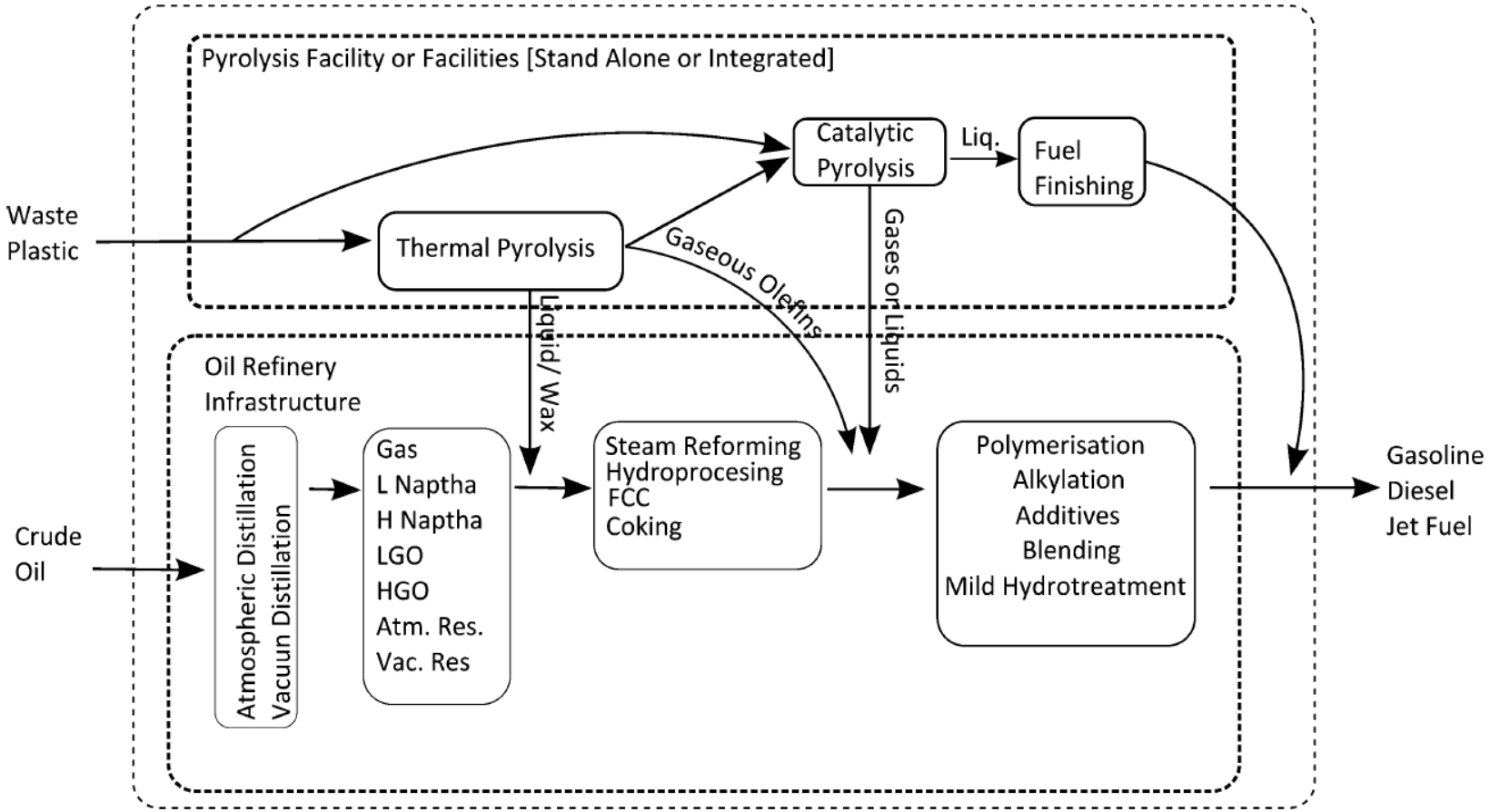

Figure 2.5 - Integrating Pyrolysis with Oil Refineries Infrastructure. Source: Butler et al. (2011).
Abb. LGO, Light Gas Oil; HGO, Heavy Gas Oil.

In conclusion, theromlysis produces monomer fractions (e.g. ethylene, propylene, styrene, butadiene, etc.) and valuable chemicals (e.g. waxes, syngas (CO + H_2), etc.). Thermolysis includes a number of processes, of which pyrolysis stands as an advanced method of recovering valuable energy (e.g. heat) and petrochemicals (e.g. naphtha, toluene, ethylene, propylene, styrene, butadiene, etc.). Pyrolysis also provides a sound solution to the lack of raw materials supplies from refineries and petrochemical complexes, as it produces naphtha, heavy oil (HO) and waxes that could be fed into steam reforming, fluid catalytic cracking (FCC) and hydroprocessing units (which exist in crude oil refineries infrastructure). These units are used to produce chemicals, additives and polymerisation units' feedstock. The residual output of char produced by pyrolysis can be used as a fuel or as a feedstock for other petrochemical processes. An additional benefit is that pyrolysis requires no flue gas clean up, as the flue gas produced is mostly treated prior to utilisation. Finally, it reduces GHGs and CO_2 emissions and provides an alternative solution to landfilling. All the above can be considered as reasons for the pursuit of research into pyrolysis of organic materials.

2.3.4. A Note on the UK Policies and Carbon Reduction Targets

The UK emits around 160 million tonnes per year of carbon into the atmosphere, of which 80% is from fossil fuel burning to supply energy demands (ACE, 2005). In 1992 the UK signed the Rio de Janeiro conference agreement to return GHGs to the 1990 level by the year 2000. This target was not achieved and in 1997 the UK agreed to cut the six main GHGs by 6% below the 1990 level between 2008 and 2012 (the Kyoto Conference agreement). This is reflected in the UK Carbon Emission Reduction Target (CERT) to make a 12.5% cut in GHGs by 2008/12 and the Climate Change Act of 2008 requirement to cut GHGs emissions by 80% below the 1990 level by 2050. OFGEM regulates the UK CERT scheme and reports suppliers' progress towards their CERT target. The UK has achieved a 12.5% reduction in the Kyoto emission limit (between 1990 to 2008/12) and a 3.3% reduction in the year 2000 from the 1990 limits, with official reports showing that it will be possible to meet the target based on current trends (ACE, 2005). This is due to the switch to gas and decline in industry emissions.

Recent reports show a government commitment to set a new target of 50% reduction by the year 2025 (LessEn, 2011). This follows a briefing made by the energy secretary Chris Huhne in May 2011, who assured that there will be a review of the UK progress in early 2014 ensuring that the country is in line with Europe. This announcement makes the UK the first country in the world to have declared a legally binding target on GHGs beyond 2020 (LessEn, 2011).

The work carried out in this thesis falls in line with the current EU directives, whereby stringent rules and regulations on waste handling, utilisation and disposal are enforced. Articles 1-29 of EC directive 2008/98, stipulates measures for environment protection by reducing the

adverse impacts of waste generation and improving efficiency of resource use (EC 2008/98, 2008). EC directive 94/62 enforces the management of packaging and packaging waste, and imposes the harmony of them both, in order to prevent environmental impacts, increase environmental protection and ensures functioning of internal markets (EC 94/62, 1994). In addition, directives EC 2002/96, EC 1999/31 and M 314, all enforce appropriate measures to minimise the disposal of waste (considered as many forms), reduce landfilling, and adopt technologies capable of recovery procedures (EC 2002/96, 2003; EC 1999/31, 1999; M 314, 2004).

2.4. Established Technologies of Pyrolysis: Pilot and Industrial Scale

Ideally, it is desirable to convert polymers (waste) into a high value refinery cuts for utilisation in petrochemical processes, e.g. light gases. In the case of PE, an interesting potential product would be a synthetic lubricant (poly-α-olefin based). This means that the product of the thermal cracking should be close to 1-decene in both chain length and molecular structure. This was the basis of the work by McCaffrey et al. (1995) on PE thermolysis in an inert atmosphere. The thermolysis of linear low density polyethylene (LLDPE) was studied at moderate temperatures (425-450°C) in a Pyrex kettle reactor, yielding a liquid product estimated as 82.5% of the initial charge to the reactor. The balance of the thermolysis reaction products was in two parts: a residue and a non-condensable gas fraction, with yields of 9.5 and 8.0%, respectively. The thermolysis of 60/40 mixtures of PE and PS was investigated at temperatures below 440°C and published in a follow up study by McCaffrey et al. (1996), where the liquid yield from the mixture of 84.1% was comparable to the yields obtained with the individual polymers. The yields of styrene monomer, 57.1%, and α-olefins, 27.7%, increased over those obtained when the polymers were processed individually. A significant interaction was observed between the polymers in which the addition of PS enhanced the rate of thermolysis of PE. Other studies focusing on products in pilot scale reactors are summarised in Table 2.3.

Table 2.3 Review of studies focusing on products yield via different isothermal set-ups of pyrolysis.

Reference	Polymers tested/Experimental setup	Notes
McCaffrey et al. (1998)	LLDPE and HDPE pyrolysis in kettle type reactor coupled with reactive distillation, yielding typical liquid product	Reactions were carried out at 440°C, under N_2 atmosphere
McCaffrey et al. (1999)	LLDPE and HDPE pyrolysis in kettle type reactor coupled with reactive distillation, obtaining conventional liquid product	LLDPE started to produce volatile products earlier than HDPE
Kaminsky et al. (1995)	1-3 kg hr^{-1} FBR pyrolysis of mixed PSW (with 0.66% chlorine)	Products contained about 36% C_2H_4, 15% C_3H_6, 9% 1-C_4H_8 and butadiene and an additional 15% pyrolysis gasoline
Mastral et al. (2002)	FBR pyrolysis of HDPE. Experiments took place at five temperatures: 650; 685; 730; 780 and 850°C were carried out and the residence time was varied from 0.64 to 2.6 s.	Main product obtained was a waxy cream coloured material (wax). The yield of this product varied from 79.7 wt% at 0.8 s to 68.5 wt%
Williams and Williams (1997)	Fixed bed static-batch reactor pyrolysis of mixed and single HDPE, LDPE, PS, PP, PET and PVC	Product yield was 9.63% gas, 75.11% oil, 2.87% char and 2.31% HCl. Gases identified were H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C and CO.
Williams and Williams (1999a)	FBR pyrolysis of PS in a temperature range of 500-700°C.	Products collected were a wax/oil condensate and a separate oil fraction. Gas content (mainly H_2 and CH_4) increased with OT.
Williams and Williams (1999b)	FBR pyrolysis of LDPE in a temperature range of 500-700°C	Gases recovered were: H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_8. Analysis of the oils showed that at the higher temperatures, the concentration of aliphatic species above about C_{30} was greatly reduced.
Bagri and Williams (2002)	Fixed bed pyrolysis of LDPE w/ zeolite catalyst	Oils recovered consisted of aliphatic compounds (alkadiene, alkene and alkane) and their branched chain derivatives
Cunliffe et al. (2003a, 2003b)	Fixed/static bed pyrolysis of polyester, phenolic, epoxy, vinylester, PP and PET.	Main products derived were: oil, gas and solid residue.
Cunliffe and Williams (2003)	Pilot static-bed reactor pyrolysis of brominated polyester/styrene	Significant effect of both the temperature and the amount of brominated resin on gas yield.

At elevated temperatures (around 850°C), PSW pyrolysis yields almost exclusively aromatics; C_2H_4 and CH_4 (Mastral et al., 2002; Mastral et al., 2003). The increase of the aromatic fraction with increasing gas phase temperature has also been reported for PSW and MSW (Day et al., 1999; Brage et al., 2000). To crack polyaromatic hydrocarbons, very high temperatures (>1200°C) and long residence times are required. Typical cracking products (e.g. H_2, C_2H_4 and C_2H_2) were also reported to increase with elevated operating temperatures by Zolezzi et al. (2004).

Many of the products yielded by pyrolysis and gasification are highly marketable. However, the fact remains that there is an even larger market now emerging for residual solids, to be utilised as carbon black or activated carbon. Although large industrial scale units do exist for both pyrolysis and gasification, most could perform more effectively if they targeted certain products depending on feedstock, market performance and demand. All such issues could be solved by end-product unit design, thereby targeting desirable products more efficiently. Thermal decomposition schemes on the end-product (employing lumped product yield) are an essential step to developing and validating industrial units targeting desirable products yielded by pyrolysis. Advances in this area will aid in the improvement of pyrolysis and gasification reactors.

One of the main technologies incorporated by a number of plants in Austria, Germany, Korea, Italy and Switzerland, is the PYROPLEQ® process. This technology (dominant in the period between 1978 to1996) is based on pyrolysis at 450-500°C in an externally heated rotary drum with gas combustion at 1200°C, and a typical feed to the process is PSW (post-consumer mixtures). A different process which has proved to be successful for PSW rich in PVC, is the Akzo process (Netherlands) (Tukker et al., 1999). This fast pyrolysis process with a capacity of 30 kg $hr^{-1}$is based on a circulating fluidised bed (CFB) system (two reactors) with subsequent combustion. Input to the process is shredded mixed waste including a high percentage of PVC waste. The main outputs consist of HCl, CO, H_2, and CH_4, and depending on the feedstock composition, other hydrocarbons and fly ash.

ConTherm® technology pyrolyses shredded fuels such as MSW and automotive shredder residues (ASR) as well as up to 50% post-consumer plastics, at 500-550°C in 100 kt/year rotary kilns supplied by TECHNIP and combusts the gas directly in a pulverised coal-fired boiler (Malkow, 2004). Residues from the process are screened and sorted to recover materials, mainly metals. The full scale industrial process of NRC® is another successful pyrolysis scheme. This process is based on pyrolysis with subsequent metal extraction technology. The aim is to produce purified calcium chloride instead of HCl and the input to the process is PVC waste (cables, flooring, profiles, etc.). No other PSW type is fed to the processing line, which results

in calcium chloride, coke, organic condensate (for use as fuels) and heavy metals for metal recycling, as products. PKA pyrolysis is another type of pyrolysis process technology, described previously by PKA (2002) and Malkow (2004). The technology comprises a modular pyrolysis and gasification concept at high temperatures. The pyrolysis takes place at 500 to 550°C in an externally heated rotary kiln and the yield is a de-dusted and homogenised CO/H_2 rich fuel gas. Char containing minerals and metals are conditioned by separating ferrous and non-ferrous metals, reduced in moisture to <10% and ground to <2 mm before being used as a fuel, a sorbent (i.e. activated carbon) or a raw material in brick production (Malkow, 2004).

The PyroMelt process (developed by ML Entsorgungs und Energieanlagen GmbH) combines pyrolysis and slagging combustion yielding an eluation-resistant, recyclable granulated slag (Juniper, 2005). The feed to the process consists of MSW, hazardous waste, ASR and post-consumer plastic waste. Pyrolysis takes place prior to the combustion process and the resulting gas is subjected to multiple scrubbing steps using pyrolysis oil. This process cools the gas from the range of 500 to 600°C down to 120 to 150°C. However, the char is cooled to 50°C and jointly combusted with a slurry composed of dust and heavy pyrolysis oils in a melt furnace (Kubota-Surface-Melt).

One of the most important pyrolysis processes is the BP polymer cracking process (Tukker et al., 1999). BP Chemicals plc has led the promotion of polymer cracking technology for chemical recycling since its beginnings in the early 1990s. After a series of pilot trials (conducted between 1994 and 1998), a plant was established in Scotland with a capacity of 25,000 tonnes/year. Figure 2.6 shows a schematic of the BP polymer cracking process. Size reduction is required for the feed, which is then fed to a heated FBR (operating at 500°C) in the absence of air. Input specifications for the process are shown in Table 2.4. Plastics crack thermally under these conditions to hydrocarbons which vaporise and leave the bed with the fluidising gas. PSW decomposition leads to HCl formation (from PVC), which is neutralised by bringing the hot gas into contact with a solid lime absorbent. For the plastic that enter the process, 85% by weight is passed on as hydrocarbon liquid and the remaining 15% is gas at ambient temperature. The gas has a high content of monomers (ethylene and propylene) and other useful hydrocarbons with only some 15% being methane (Brophy et al., 1997). Total solids produced are typically up to 0.2 kg/kg of total solids feed.

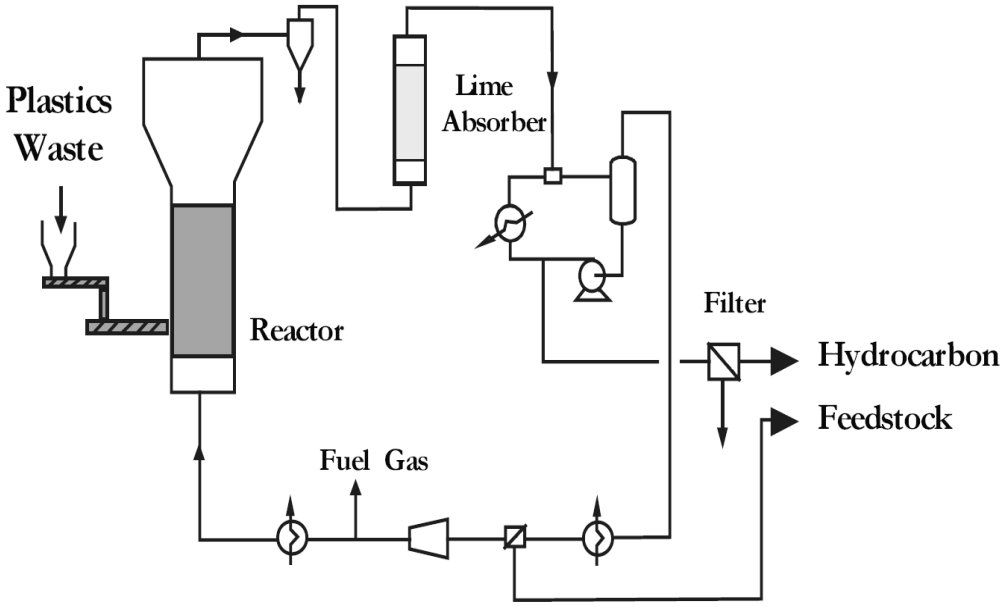

Figure 2.6 - BP polymer cracking process schematic. Source: Tukker et al. (1999).

Table 2.4 BP polymer cracking process input specifications.
Source: Tukker et al., 1999.

Material	Unit	Normal	Limit
Polyolefins	wt%	80	min. 70
PS	wt%	15	max. 30
PET	wt%	3	max. 5
PVC	wt%	2	max. 4
Total Plastic Content	wt%	92	min. 90
Ash	wt%	2	max. 5
Moisture	wt%	0.5	max. 1
Metal pieces	wt%	-	max. 1
Size	mm	1-20	
Fines sub-250 micron	wt%	-	max. 1
Bulk Density	kg m^{-3}	400	300

One of the main pyrolysis technologies is the BASF process (Figure 2.7). This process started with a pilot plant capacity of 15,000 tonnes/year in Ludwigshafen, Germany, in 1994. As is the case with many recycling schemes, the BASF process starts with a pre-treatment step, whereby the mixed PSW is ground, and separated from metals and agglomerated materials (Heyde and Kremer, 1999). The conversion of the PSW into valuable petrochemicals takes place in a multi-stage melting and reduction process. In the first stage the plastic is molten and de-halogenated to preserve the subsequent plant segments from corrosion. The hydrogen chloride separated out in this process is absorbed and processed in the hydrochloric acid production plant, and hence the major part of the chlorine present in the input (e.g. from PVC) is converted into saleable HCl. Minor amounts are available as NaCl or $CaCl_2$ effluent (Heyde and Kremer, 1999). Liquefied plastic waste is heated to over 400°C and cracked into

components of different chain lengths producing gases (20-30%) and oils (60-70%). Naphtha produced by the feedstock process is treated in a steam cracker, and the monomers (e.g. ethylene, propylene) are recovered. High boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use.

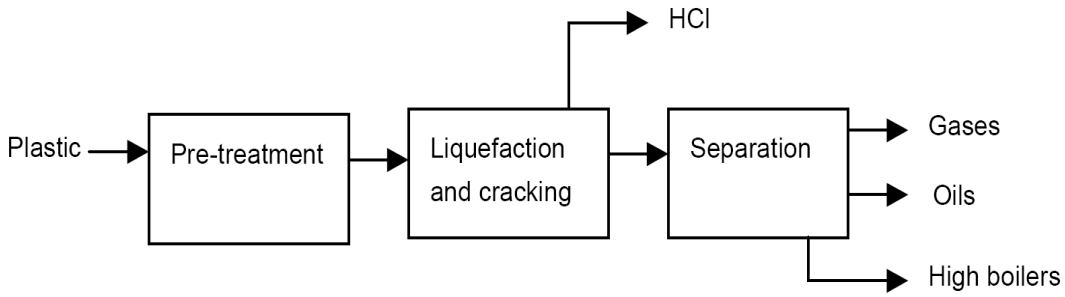

Figure 2.7 - BASF pyrolysis process. Source: Tukker et al. (1999).

An alternative technology that has proved to be very successful for PSW treatment (especially for the case of PVC cable waste) is the NKT process (Figure 2.8). This process is based on an initial pre-treatment step that involves separating light plastics (PP, PE, etc.) and other materials, e.g. wood, sand, iron, steel, brass, copper and other metallic pollutants. The PSW waste is then fed to a reactor at a low pressure (2-3 bars) and a moderate temperature (375°C). The process does not emit dioxins, chlorine, metals or plasticisers and there are no liquid waste streams in the process since all streams are recycled within the system. A small volume of carbon dioxide gas is formed by the reaction between lime/limestone and hydrogen chloride. Mixed PVC building waste containing metals, sand, soil, PE, PP, wood and rubber waste has been successfully treated. Other smaller scale pyrolysis processes are also available and operated for chemical treatments, and Table 2.5 summarises these pyrolysis processes and their current status.

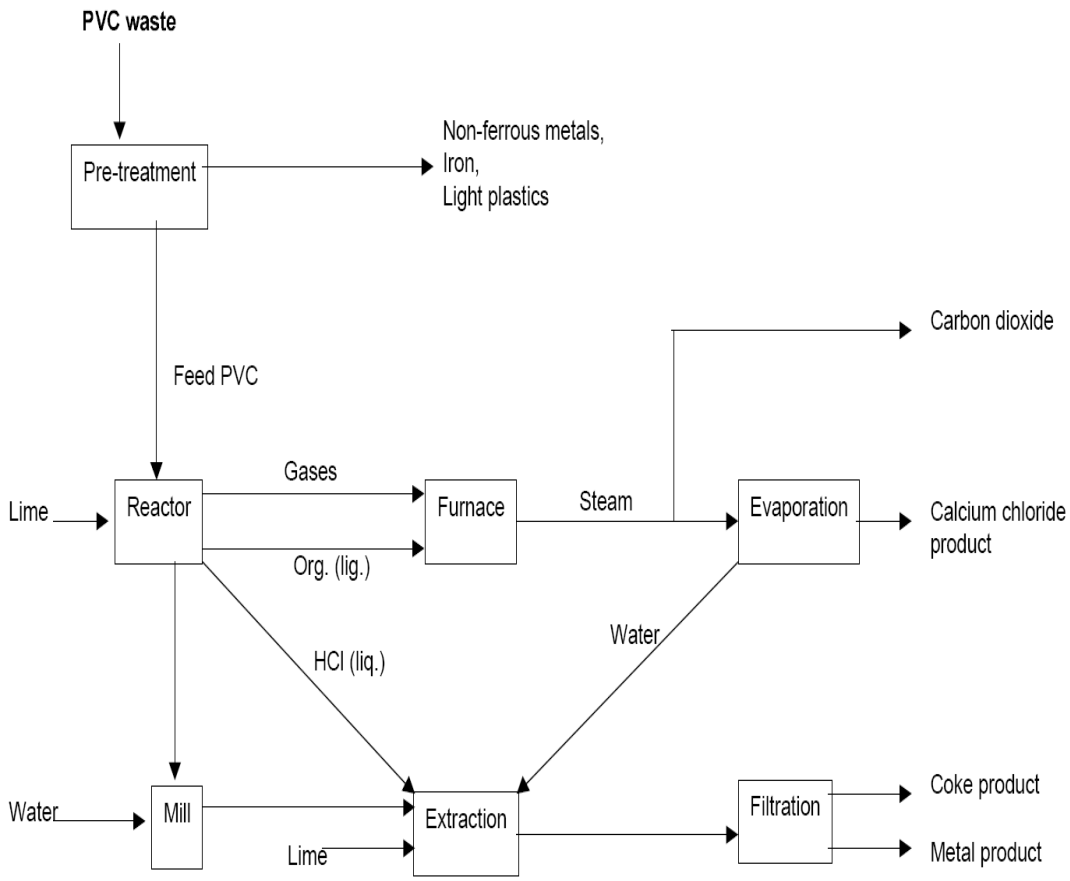

Figure 2.8 - NKT process diagram.
Source: Tukker et al. (1999).

Table 2.5 Summary of other pyrolysis processes, their operating conditions and current status.

Technology name	Operating conditions	Notes	Reference
KEU process	T_{op}=350-550°C Input: PVC waste (palletised) Output: Slag, dust and energy	Pyrolysis in a vertical reactor Char produced is burned in a rotary drum incinerator	Buhl, 1999.
Wayene	T_{op}=900°C Input: PE, PP, PS Output: 75-89% medium oil, 15-20% light oil	High temperature pyrolysis Proven capacity: 50 tonnes/day	Tukker, 1999
Toshiba	Input: PSW with 20% chlorine content (powder) Output: 90% oil P_{op}= > 10 atm T_{op}=650-750°C	Reports show technology in research stage.	Tukker, 1999
Berliner process	Input: PSW Output: 5% cokes, 2% metals, 3% inert solids, 38% BTX and light fraction, 3% medium fraction and gas	Pilot scale Proven capacity: 20,000 tonnes/year	Tukker, 1999
Noell	T_{op}=650-750°C Input: PSW, 65% linear, 20% cyclic and 15% PVC. Output: Slag, dust and energy	Industrial scale and capacity proven.	Tukker, 1999

The most applied within this group of processes is the Noell process, for its ability to convert 25% of the feedstock to oil (Tukker et al., 1999). The process operates in a rotary kiln reactor with a 250 kg m^{-3} density for the feed. It is also worth mentioning that the pyrolysis process is rapidly gaining importance for polyolefin feedstock and polyurethane (PU) foams. Zia et al. (2007) reported the PU pyrolysis resulting from automobile seats and other end products, and a two zone pyrolysis reactor has also been suggested for PU char processing.

A fresh industrial perspective on pyrolysis was discussed by Butler et al. (2011), in which the technology as a whole is put alongside mechanical treatment and incineration as a complementing waste management component (rather than a competing technology) in what is known as the cascade waste management concept (Figure 2.9). The MSW fraction is divided

into two streams; the pyrolysis suitable stream will not only contain plastics, but will also include the fractions that waste mechanical treatment facilities cannot deal with.

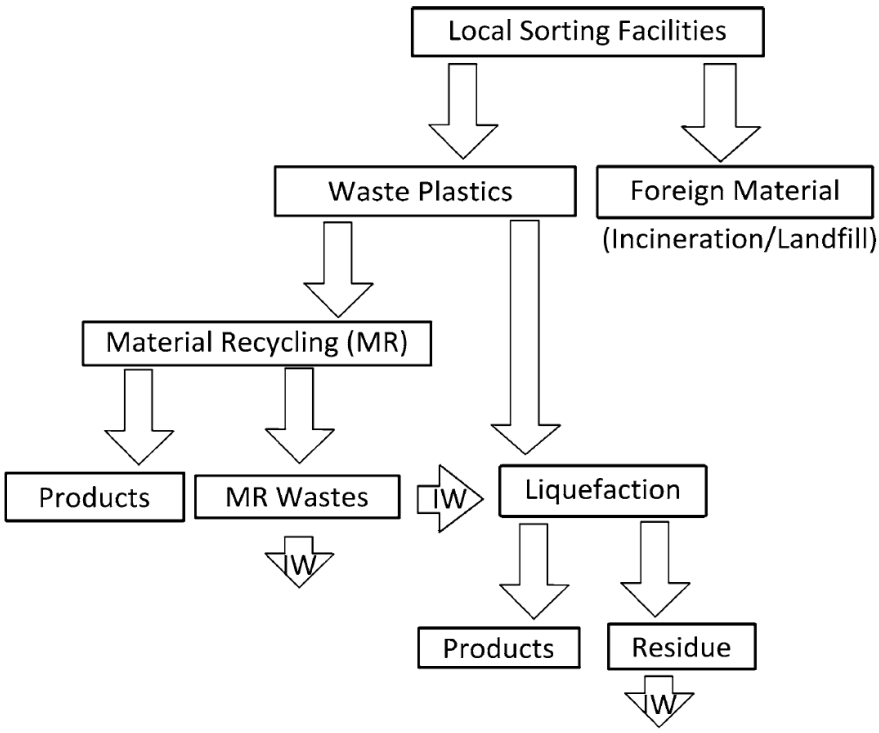

Figure 2.9 - The cascade waste management concept as illustrated by Butler et al. (2011).

2.4.1. Gasification

Thermolysis technology covers gasification, in which air is used in a sub-stoichiometric ratio as a gasification agent to produce high calorific fuels (CPPIA, 2007). The main advantage of using air instead of O_2 alone is to simplify the process and reduce costs. However, a disadvantage is the presence of N_2 (inert) in air which causes a reduction in the calorific value of the resulting fuels due to the dilution effect on fuel gases. Consequently, steam is introduced in a stoichiometric ratio to reduce the presence of N_2. Several types of gasification processes have already been developed and reported; however, their practical performance data have not necessarily been satisfactory for universal application.

A significant amount of char is always produced in gasification which needs to be further processed and/or burnt. Other gasification schemes (mainly on the pilot scale) use a great deal of expensive pure oxygen, whilst others necessitate considerable amounts of expensive materials such as coke and limestone, and deposit much sludge from which metals cannot be separated. An ideal gasification process for PSW should produce a high calorific value gas, completely combusted char, a metal product which can easily be separated from ash and should not require any additional installations for air/water pollution abatement.

Gasification attempts have been reported since the early 1970s (Hasegawa et al., 1974; Buekens, 1978). The gasification into high calorific value fuel gas obtained from PSW was demonstrated in the research stages and results were reported and published in the literature for PVC (Borgianni et al., 2002), PP (Xiao et al., 2009) and PET (Matsunami et al., 1999). In addition, a need to utilise as much waste as possible to treat in co-gasification is something that has captured the attention of many researchers. Table 2.6 summarises the main gasification technologies available to treat and/or co-gasifiy PSW.

In its industrial application, the feasibility of co-gasification for a number of waste streams (PSW, biomass, RDF, etc.) has been proven. A typical co-gasification scheme will include a two-step process of two adjacent gasification furnaces (Conesa et al., 1996; Ranzi et al., 1997; Zia et al., 2007). After pre-treatment (i.e. shredding), the mixed stream will be introduced to an RDF moulder in which air sorting takes place and steam treatment. Oxygen and steam will be introduced to the first gasifier operating at low temperatures (outlet steam temperature of 1300°C) with circulating sand at a temperature around 700°C. In the second-stage high-temperature gasifier, the gas from the low- temperature gasifier is reacted with steam typically at a temperature of 1500°C to produce a gas composed primarily of carbon monoxide and hydrogen. At the furnace outlet, the gas is rapidly cooled to below 200°C to prevent the formation of dioxins and chlorides (based on chlorine content on PSW). The granulated blast furnace slag also produced is used in civil engineering and construction materials. The gas then passes through a gas scrubber, and any remaining hydrogen chloride is neutralised by alkalis and removed from the synthetic gas. This synthetic gas is used as a raw material within the chemical industry to produce chemicals such as hydrogen, methanol, ammonia and acetic acid.

Table 2.6 Summary of main Gasification technologies reported on PSW.

Technology	Summary	Reference
WGT process	Different types of wastes (PSW, MSW, sludges) are mechanically pre-treated, sorting out incombustibles and granulated to optimum sized particles and fed into a cylindrical reactor for gasification at 700-900°C to yield a HCV gas. Upon discharge and subsequent separation of gas and char, the latter may be utilised via combustion in a boiler to raise steam.	WGT, 2002
Texaco process	PSW is mildly thermally cracked (depolymerisation) into synthetic heavy oil and some condensable and non-condensable gas fractions. The non-condensable gases are reused in the liquefaction as fuel (together with natural gas). The gasification is carried out with oxygen and steam at a temperature of 1200 – 1500°C.	Weissman, 1997; Croezen and Sas, 1997
SVZ process	Input is fed into a reactor (kiln), together with lignite (in the form of briquettes) and waste oil. Oxygen and steam are used as gasification media, and are supplied in counter flow with the input materials. Liquid hydrocarbons are further processed by oil pressure. The gas is used mainly for methanol production and around 20% is used for electricity production.	Tukker, 1999
Akzo Nobel	The process consists of two separate circulating fluid bed (CFB) reactors at atmospheric pressure. The first is a gasification reactor in which waste (usually rich with PVC) is converted at 700-900°C into product gas (fuel and HCl gas) and tars. The second unit is a combustion reactor that burns the residual tar to provide heat for the gasification process. Circulating sand between the gasifier and combustor transfers heat between the two reactors.	Tukker, 1999

2.4.2. Hydrogenation

Hydrogenation (hydrocracking) by definition means the addition of hydrogen (H_2) by chemical reaction (March, 1992). Many technologies employing PSW hydrogenation have failed or been abandoned during the pilot stages. The RWE process was one of these terminated projects which employed hydrogenation following the depolymerisation of plastic waste (10 kg hr^{-1}), and HCl was removed afterwards for contaminated PSW. The RWE process operated in a temperature range between 400 to 500°C and the main outputs were 80% oil, 10% gas and solids. The Hiedrierwerke and Freiberg hydrogenation processes are two other examples of technologies currently terminated for financial reasons. Both processes employed a hydrocracking reactor above 400°C to produce rich oils (Nishino, 2005).

The main technology applied in PSW recycling via hydrogenation technology is the Veba process. Based upon the coal liquefaction technology, Veba Oel AG® converted coal by this process into naphtha and gas oil. The current PSW treatment technology employs a depolymerisation section where the agglomerated plastic waste is kept between 350-400ºC to effect depolymerisation and dechlorination (in the case of PVC rich waste). The overhead product is partially condensed (Horvat and Ng, 1999) and contains 18 % of the chlorine input; this is fed into a hydrocracker where the HCl is eliminated through the formation of water. The resulting Cl-free condensate and gas are mixed with the depolymerisate for treatment in the VCC section. The main outputs of the process can be summarised as follows: (i) HCl, (ii) Syncrude from the VCC section (chlorine free), (iii) Hydrogenated solid residue, and (iv) Off gas. The input for the depolymerisation section was described by Sas (1994) as follows: (i) Particle size < 1.0 cm, (ii) Bulk density ≥ 300 kg m^{-3}, (iii) Water content < 1.0 wt%, (iv) PVC < 4% (≤ 2 wt% chlorine), (v) Inert content < 4.5 wt% at 650 ºC, (vi) Metal content < 1.0 wt%, and (vii) Content of plastic ≥ 90.0 wt%. This should not to be confused with the Veba Combi Cracking (VCC) process which is described in Chapter 6.

2.4.3. Treatments of a Chemical Nature

In this section, other treatments of either a pure chemical nature or other (non-thermolysis) schemes employing polymer degradation technologies are detailed. One of the main technologies emerging from the 1980s is the degradative extrusion process, where plastic is degraded in an extruder for recovering certain chemicals.

This process employs high operating temperatures and influences PSW degradation via mechanical and chemical energy (Michaeli and Lackner, 1995) and degradation promoting additives may be employed. The IKV process is one of the main technologies used in degradative extrusion, and the input to the process is PSW with a maximum PVC content of

80%. The operating temperature is between 300 to 400°C, employed in a pilot scale twin screw extruder (Brandrup et al., 1996). Other technologies employed are the Leuna and Stahlwerkke processes, with a 400 and 200 kg hr^{-1} capacity, respectively. Both processes operate in the range of 400°C for PSW with up to 50% PVC content.

Another advantageous technology for use in chemical treatments is catalytic and steam cracking. The concept for both processes is the employment of either steam or a catalyst in a unit operation and Table 2.7 summarises the main technologies employed in steam and catalytic cracking of PSW. Whilst degradative extrusion, steam and catalytic cracking are employed worldwide, thermoplastics (mainly polyolefins) are advantageous for other recovery methods that are present in both pilot and industrial schemes. These schemes fall into the category of chemical recycling, and can be subdivided into feedstock (monomer) recycling and recycling of a chemical nature.

Recycling PSW via pure chemical routes can be summarised by the following technologies: hydrolysis, glycolysis, fractionation, hydroglycolysis, aminolysis, methanolysis and acid cleavage. Table 2.8 summarises chemical recycling schemes, which fall outside the advanced TCT category.

Table 2.7 Summary of main steam and catalytic cracking technologies employed in PSW chemical recycling.

Technology name	Process conditions	Notes	References
Fuji process	T_{op}= 400°C, T_{ip}= 250°C Capacity (pilot): 500 ton/yr Capacity (input): 5000 ton/yr	Industrial scale Low temperature catalytic cracking Employing pyrolysis technology Zeolite catalysts are used (ZSM5) Input: Polyolefin waste Output: 80% oil, 15% gas & 5% solid rest fraction	Brandrup et al., 1996; Tukker et al, 1999
Kentucky process	T_{op}= 400-450°C, P= 56 atm Input: PSW Output: 90% oil	Developed in the University of Kentucky (US) Research stage Zeolite catalysts are used	Tukker et al, 1999
Leuna degradative extrusion + steam cracking process	T_{op} (extrusion) = 400-500°C, T_{op} (extrusion)= > 800°C Input: 13 wt % PSW Output: C_2, C_3 and C_4 monomers	Description: light PSW fraction is treated with degradative extrusion and then mixed with paraffin from hydrocracking. This mixture is the input for steam cracker. Project showed good results but terminated due to lack of interest.	Tukker et al, 1999
Amoco	T_{op}= 490-580°C Input: PE, PP, PS, PSW mixed with vacuum gas oil Input quality: in solution Output: Naphtha, light mineral oil	Research	Horvat and Ng, 1999

Table 2.7 (Cont'd) Summary of main steam and catalytic cracking technologies employed in PSW chemical recycling.

Mazda	Input: Shreded PSW from scrap car parts. Output: 60% (oil + kerosene)	Pilot	Horvat and Ng, 1999
Nikon	T_{op}= 200-250^{o}C Input: PSW (10 mm in size) Output: 80% oil	Pilot Metal catalyst are employed Research	Horvat and Ng, 1999
Molten Metal Technology	T_{op}= 1400^{o}C Input: PSW and organic waste Output: synthesis gas, HCl, slag	Nickel based catalyst are used 30% HCl has been recovered in lab scale	Blengini, 2009

PC: process conditions, T_{op} (^{o}C): operating temperatures,
T_{ip} (^{o}C): input temperatures

Table 2.8 Summary of chemical and monomer (feedstock) recycling schemes of a non thermo-chemical nature.

Technology name	Process conditions	Notes	References
PET Hydrolysis	T_{op} = 200°C P = 2-5 MPa	PET is heated with an excess of water at high temperatures	APC, 1999; Brandrup et al., 1996; SubsTech, 2006
PU Hydrolysis (Bayer General Motors)	-	Pilot scale	APC, 1999; Brandrup et al., 1996; SubsTech, 2006
PA 6 treatment via tehromlysis/hydrolysis	T_{op} = 300°C P = 20-100 bar	Depolymerization (monomer) recycling with water at high temperatures	SubsTech, 2006
Methanolysis of PET	T_{op} > 200°C P > 2 MPa	Metal catalysts are applied in this process Insensitive to contaminants	Mastellone, 1999
Glycolysis of PET	T_{op} > 200°C	Acceleration with catalyst	SubsTech, 2006
PMMA depolymerization	T_{op} > 300°C	Molten baths used (tin and lead) Several minutes residence time	SubsTech, 2006; Recovinyl, 2008
Acid cleavage of PA 6	Phosphoric acid medium used	Industrial scale	SubsTech, 2006

2.5. Energy Recovery: Quaternary Treatments of Plastic Solid Waste via Combustion Processes

Economic constrains pose a major dilemma in industry, especially for recovery methods which process scrap and heterogeneous waste streams. Energy recovery offers a solution to such problems by employing combustion processes to produce heat, steam and/or electricity. PSW has a high calorific value when compared to other materials due to its crude oil origins, as Table 2.1 illustrates by comparison to gas oil, heavy oil and other crude oil derivatives. Since the heating value of plastics is high, they make a convenient energy source, and producing water and carbon dioxide upon combustion makes PSW similar to other petroleum based fuels. Chemical treatment of polymers, namely via pyrolysis, produces valuable chemicals and energy in the form of heat. This is considered one of the main advantages of pyrolysis and a reason for it being higher up the hierarchy than quaternary treatment methods. In this thesis, an incineration unit (IU) with combined heat and power (CHP) is included in the LCA study conducted in Chapter 6. Consequently, for completeness this section focuses on combustion processes as a possible route for MSW treatment.

Energy recovery (quaternary treatment) methods include incineration under controlled conditions. This generates electricity in addition to reducing the volume of the waste. Excess heat produced in a plant can then be used in industrial or household heating schemes and this is known as a CHP scheme. The majority of incinerators in the UK employ moving grate technology, whereby a mechanical grate propels the waste into the furnace. In general, incineration of PSW results in a volume reduction of 90-99%, which reduces the need for landfilling. In the process of energy recovery, the destruction of foams and granules resulting from PSW also destroys chlorofluorocarbons (CFCs) and other harmful blowing agents present (APC, 1999). However, the presence of fire retardants (FRs) increases the complexity of energy recovery from waste.

Dependency on fossil fuels as an energy source could be reduced by PSW utilisation in energy recovery schemes. It is estimated that by 2020, 17% of the UK's electricity could come from waste compared to the 0.5% reported (Yassin et al., 2007). The Department of Environment, Food and Rural Affairs (DEFRA, UK) published a review in 2006 on England's waste strategy and set a target of 25% MSW to be used in EfW, which corresponds to 700 MWe of electric capacity. Further to the DEFRA review, many associated agencies embraced the idea of direct incineration and the recovery of energy by thermal processing. Three new EfW plants in Hampshire accounted for 46% and 35% of its MSW and recycling capacities in 2004-2005, and a new EfW plant to treat 500,000 tonnes per year is under construction in Kent. In Sheffield, the existing EfW plant, with a capacity of 135,000 tonnes, is being replaced by a new

plant with a capacity of 225,000 tonnes (Ares and Bolton, 2002; Yassin et al., 2005; Quant, 2005; Yassin et al., 2007). It should also be stated that PSW as a feedstock has two main objectives within the incineration industry: (i) to act as fuel to supply energy in its subsequent combustion phase, (ii) to act as a reducing agent in pyrolysis and gasification processes to replace coke (Westerhout et al., 1998b). Over the past decade, enviro-friendly chemical recycling processes have become of interest, and in the steel making industry the use of waste plastics as a supplemental fuel with coal has been explored (Janz et al., 1996; Ariyama, 1996).

2.5.1. Co- Incineration of Plastic Solid Waste

MSW can be accepted with high fractions of PSW in municipal solid waste incinerators (MSWIs). However, for such combustion processes to be applicable to PSW a number of issues arise. First, if one wants to produce reusable slags, the heavy metal input into the incinerator should be limited (March, 1992; Kowalska et al., 2002). Furthermore, an important point is the relatively low incineration temperature of MSWIs (around 850 ºC). Fluidized bed combustors (FBCs) are increasing in popularity for incineration due to; (i) less complex emissions control systems, (ii) high combustion efficiency with simple operation and a fast response, (iii) reduction in boiler size, and (iv) low corrosion with easier ash removal. Yassin et al. (2007) reviewed FBC technologies in Europe, where the revolving fluid bed developed by Ebara Co. is stated as being very rapidly utilised on the continent. More than 100 units are installed worldwide, including the Madrid plant unit which takes 10% of the city's waste (with 9% commingled PSW) to produce electricity. The main principle for this technology is the mechanism of the internal furnace with no moving parts, which is equipped with a slanted bed floor to produce a revolving sand motion.

Germany has the highest number of incinerators in Europe, with over 53 units with a capacity exceeding 10.7 million tonnes/year (Pollution Issue, 2007). In the USA, the design capacity (110 tonnes/day) of over 190 incinerators had been exceeded in 2006. In the EU, ISOPA (European Diisocyanates & Polyols Producers Association) supports the incineration of MSW with a high content of PSW (which make up on average 7% of MSW), which results in a high calorific value fuel with constant ash content (API, 2007).

Many countries within the EU cover the electrical demand to hundreds of communities by direct incineration, e.g. Denmark, Sweden, and Germany. In the UK, DEFRA announced that currently 15 EfW plants exist in the UK with a design capacity exceeding 3 million tonnes of municipal waste (DEFRA, 2006). Co-incineration is also employed to generate energy and reduce air pollutants emission control problems. A number of European nations have adopted a strategy of mixing high content PSW residues with coal, capitalising upon the concept of economies of scale, yet still transportation issues arise in this case. Normally, it has been

demonstrated that fuels from waste within a distance of 80 km could support, at the maximum, a 20 MW power plant, and this may be sufficient for industrial applications. A previous study by Boavida et al. (2003) investigated the co-combustion of PSW with coal using a FBC with the aim of achieving a fuel mixture with little variation in its heating value and simultaneously upgrading the mixture for energy purposes. The results indicated that the form in which the fuel is fed into the combustor significantly influences the combustion performance. Differences were observed in terms of the combustion efficiency and emissions when waste was fed in a densified or a fluffy state, or when mixed with coal. Part of the combustion of the waste material, contrary to that of coal, was observed to take place in the freeboard where the temperature was as much as 150°C above that of the bed. The addition of waste by 20% in weight was found to cause little disturbance in the bed temperature but relatively more enhanced variations in the freeboard, due to an increase in volatiles released.

2.5.2. Blast Furnaces and Cement Kilns

Many industrial schemes utilise cement kilns as incinerators. The cement industry has been using alternative fuels made from PSW for over two decades. Figure 2.10 illustrates schematically the concept of cement kiln processing of waste with a high PSW content.

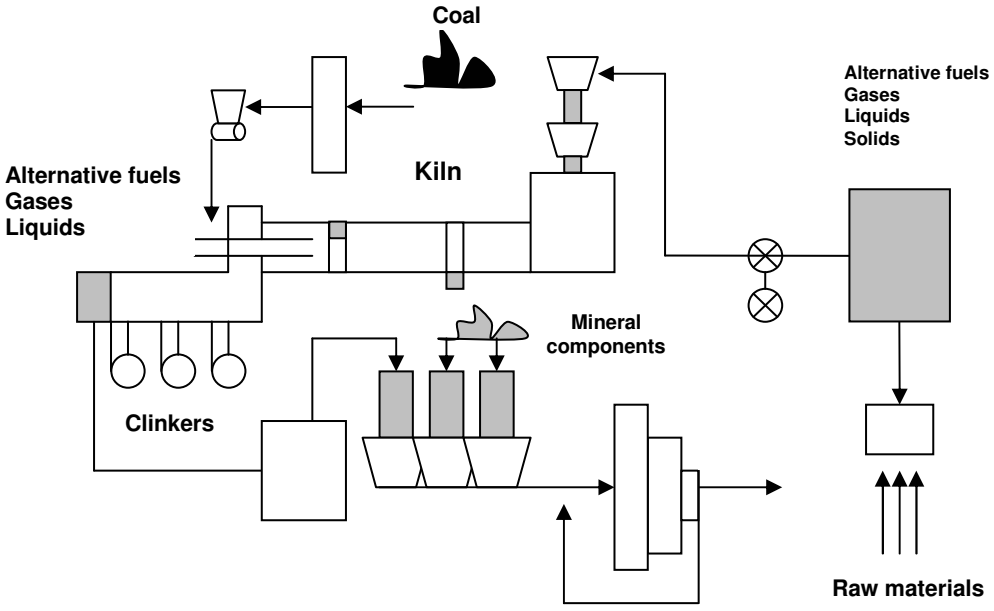

Figure 2.10 - Schematic of cement kiln combustion (McDoughall et al., 2008).

The technological requirements of this industry make it particularly well suited to the incineration of fuels made from waste. Cement kiln operation lines are especially suitable for the use of PSW as a feedstock (Tukker et al., 1999). The incineration conditions in cement kilns make them suitable for using alternatives fuels made from PSW because of the following

factors: a high temperature, a sizeable kiln length, fuel remaining in a kiln for a long time, and the alkaline environment present within the kiln. Temperatures in the kiln are very high (the gas temperature in the combustion zone reaches 2000°C), and the gas residence time in temperatures around 1200°C is about three seconds given a 2-3% oxygen content in the gases. These conditions are far above the temperature level and time necessary for the total combustion of high molecular hydrocarbons. There are 250 cement plants within the EU producing 170 million tonnes of cement per year (Janz and Weiss, 1996). In Poland there are 12 full-production cycle cement plant and Poland produced almost 11 million tonnes of cement in 2003. According to recent estimates, the greatest usage of alternative fuels in European countries is to be found in Holland (72%), Switzerland (34%) and Belgium (30%) (Tukker et al., 1999).

Many cement kilns in the UK, Belgium, Holland, Switzerland and other countries have therefore started to use pre-treated waste streams as a fuel. One example is the cement plant owned and operated by Lafarge cement S.A. (Poland) using alternative fuels made from processed waste. In addition, the solid materials flow in the opposite direction to the incineration gases and the length of the kiln (200 m) results in a long residence time of incineration gases at high temperatures: 4 to 6 seconds at 1800°C and 15 to 20 seconds at 1200°C (Horvat and Ng, 1999). Two processes are dominant in this application; a dry process and wet combustion. In the dry process the raw materials are introduced in dry form into the kiln and in the wet process, these materials are introduced in the form of slurry. The type of process used depends, amongst others things, on the source of the kiln's raw materials. A clear disadvantage of the wet process is that it needs much more energy than the dry process (5,000 MJ/tonne against 3,600 MJ/tonne, respectively), since no water has to be evaporated in the dry process. In the canton of Zug (Switzerland) more than 30 fractions of waste are collected and sent for incineration outside the canton (Edelmann et al., 2005). In the period between 1995 until 2000, all commingled PSW was send to the cement kiln of Untervaz. In 2001, the efficiency of the kiln was increased by 10% by altering the feed and recycling plastic bottles and containers from collection points. By 2001, 50% of all plastic waste was collected separately for cement production.

Out of the different recycling technologies, recovery of energy and fuel from polymers is a very important and effective option. For the smelting of iron ore for pig iron production, coke is traditionally used in a blast furnace to generate CO and heat. PSW has replaced part of the coke or pulverised coal for pig iron production. Energy and chemical recycling processes have been developed worldwide to treat PSW via blast furnaces as a reducing agent for coal or coke implementing pyrolysis, gasification, a combination of both in a step wise fashion or combustion. This technology has been dominant in a number of markets and industries

worldwide and has been reported by a number of steel manufacturers, including the Bremen Steel Company in Germany and Pohang Iron and Steel Making Company in Korea (PISMC, 1996a; 1996b, Asanuma et al., 1997).

Current regulation in the EU and North America require 25% of the waste stream to be separated for recovery prior to incineration. However, this percentage varies from one country to another depending on the materials and amount of it in the final MSW line (USEPA, 1991). The US and EU regulations cover the main three types of MSWIs which can be classified as follows (depending on airborne emissions and feed processed):

1. Mass Burn Combustors (MBCs): These incineration units process over 55% on average of the MSW in the EU and the US. MBCs accept all MSW except items that won't go through the feed line. Non-segregated refuse is placed on a grate that moves through the combustion chamber. Air is used in excess and is forced below and above the grate.

2. Refuse Derived Fuel Combustors (RDFCs): These units require the waste to be processed prior to combustion. Processing typically includes shredding and removal of non-combustibles. RDFCs maybe co-fired with coal.

3. Modular combustors: These combustors are the smallest in size and types vary in operation mode and percentage of excess air.

Despite the relatively low contribution of PSW by weight to the MSW final stream, plastics contribute 25% to the total calorific value of the MSW content (Magee, 1989). Plastics (commercial grades, resin, master batches and pure polymers) all combust in two phases, a pyrolysis and a combustion phase (Figure 2.11).

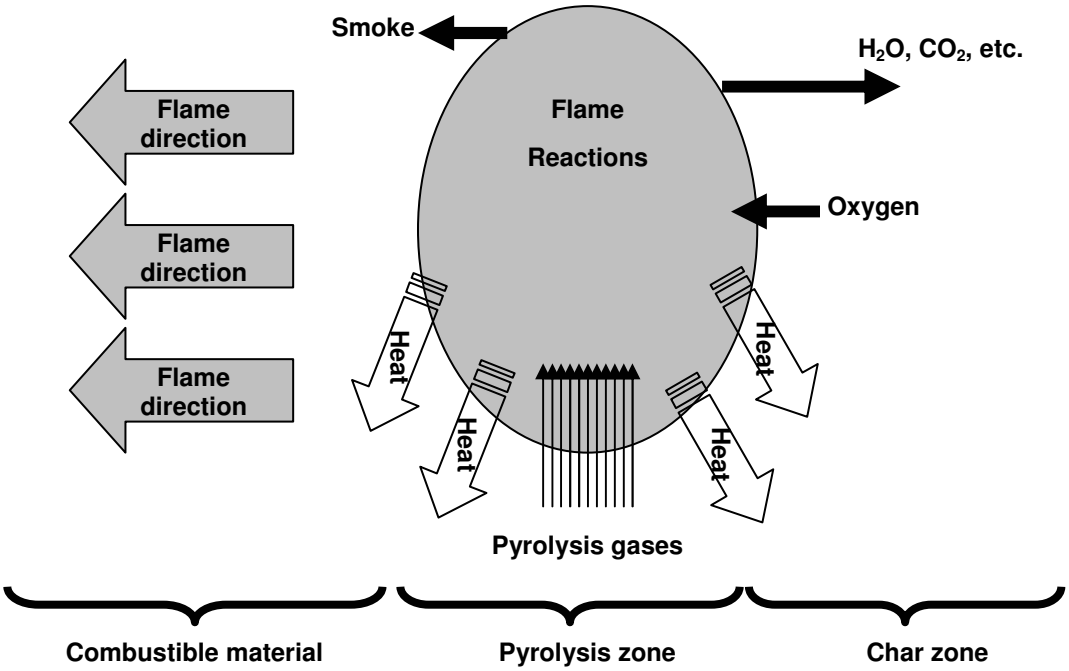

Figure 2.11 - Flame dynamics showing separation of pyrolysis and oxidation (Wark et al., 1998).

In the first phase, the plastics decompose chemically by heat into gases, the composition of which strongly depends on the polymer types, contents, and on the incineration process condition (temperature, pressure, etc., Boettner et al., 1973). The mixture of gases then enters the flame where combustion occurs. Regardless of the type of plastic materials combusting, gases from combustion processes are typically small and stable (two to three atoms) (Dynamac, 1989) and include H_2O, CO_2, NO, CO and SO_2. Incomplete combustion caused either by an insufficient amount of oxygen or a low flame temperature may lead to the emission of more complex compounds. Generally, the most concern in MSW incineration processes is regarding compounds resulting from incomplete combustion, e.g. chlorobenzene. Incomplete combustion can also lead to the release of certain amounts of particulates (soot), which may also disrupt the operation of the particulate collection devices.

In conclusion, TCT technologies have been implemented in industry targeting rich refinery cuts and petrochemicals. Operating conditions, feedstock and unit type are the major factors that differentiate between technologies and product yields. At elevated temperatures (around 850°C), PSW pyrolysis yields almost exclusively aromatics, C_2H_4 and CH_4 (Mastral et al., 2002; Mastral et al., 2003) and an increase in the aromatic fraction with increasing gas phase temperature has also been reported for PSW (Day et al., 1999; Brage et al., 2000). To crack polyaromatic hydrocarbons, very high temperatures (>1200°C) and long residence times are required. Typical cracking products (e.g. H_2, C_2H_4 and C_2H_2) have also been reported to

increase with elevated operating temperatures (Zolezzi et al., 2004). In PSW pyrolysis and gasification, endothermic reactions involving steam and CO_2 (Franco et al., 2003; Marquez-Montesinos et al., 2002) and high heating rates, create a char which is more reactive and easier to deal with than char produced from other thermal processes (Zanzi et al., 1996; Zanzi et al., 2002). As a result of these reactions, a high reaction temperature has been reported to increase the H_2 concentration (Lv et al., 2004), gas yield (Pinto et al., 2002) and sometimes LHV (Narvaez et al., 1996) for a wide range of gasification configurations and oxidising media.

Other thermolysis technologies (gasification, hydrogenation), treatments of a chemical nature (glycolysis) and combustion processes (incineration) were also reported. PSW incineration leads to a volume reduction of 90-99%, which reduces the reliability on landfilling. In the process of energy recovery, the destruction of foams and granules resulting from PSW also destroys CFCs and other harmful blowing agents present (APC, 1999). In incineration processes, the temperature is an essential parameter that leads to a reduction in CO and N_2O accompanied with an increase in NO_x. The addition of waste material is found to reduce N_2O while enhancing NO_x formation and this is believed to be due to the release of fuel-N from waste materials being mostly NH_3 groups. The conversion of fuel-N to NO_x varied from 4 to 6% and this is below what is usually observed in fluidised beds. Finally, thermolysis technologies (namely pyrolysis) alongside incineration units have a number of established technologies that present themselves as an advantageous route for chemical and energy recovery for treating a wide spectrum of feedstocks.

2.6. Thermal Cracking & Weight Loss (Degressive) Kinetics

An optimum TCT process is a process that recovers energy, concurrently recovers valuable products and solves the disposal problem (i.e. landfilling). A lack of fundamental data (e.g. the behaviour of materials being treated at different operating conditions, product yields and purity, etc.) hampers the optimal design and operation of pyrolysis reactors, hence the importance of kinetic studies (Oh et al., 2003). Understanding the behaviour of polymeric materials during their thermal degradation in the presence of inert (i.e. nitrogen, helium, argon, etc.) or partial oxidative atmospheres can aid in the understanding of pyrolysis, combustion and other thermal processes. The thermal decomposition of polymeric and lignocellulosic materials is a complex process which involves a number of chemical reactions as well as physical stages such as heat and mass transfer (Bilbao et al., 1997). This section focuses on the degressive behaviour of polymers subjected to pyrolysis and the different mathematical expressions derived to evaluate the kinetic parameters of the reactions.

Thermal degradation of organic materials allows the collection of a number of the constituting chemicals, combustible gases and/or energy, with the reduction of landfilling as an added advantage (Mastral et al., 2007). Pyrolysis is an advanced conversion technology that has the ability to produce a clean, high calorific value gas from a wide variety of feed streams. The hydrocarbon content of the feed is converted into a gas, which is suitable for energy production without the need for flue gas treatment. Pyrolysis is capable of treating many different solid hydrocarbon based wastes whilst producing a clean fuel gas with a high calorific value, typically between 22-30 MJ m^{-3}, depending on the waste material being processed. A lower calorific value is associated with biomass waste, and a higher calorific value is associated with other wastes such as sewage sludge (Prestige Thermal, 2007).

Gases can be produced with higher calorific values when the waste contains significant quantities of synthetic materials such as rubber and plastics. Solid char is also produced from the process, which contains both the carbon and the mineral content of the original feed material. The char can either be further processed onsite to release the energy content of the carbon, or utilised offsite in other thermal processes. Pyrolysis has been employed by a number of researchers to treat PSW or other waste, including biomass and rubbers (Ray et al., 2004; Yang et al., 2004) and TCT processes allow combustible gases and/or energy to be recovered whilst also reducing landfilling. Implementing these processes for a commercial scale reactor requires knowledge of the thermal degradation behaviour of the materials under different operating conditions.

In polyolefins upgrading thermogravimetric analysis (TGA) is the most common technique used for thermal degradation on a micro laboratory scale, although it is often carried out at temperatures below 450°C. Consequently, extrapolating the results to the design of the reactors operating at higher temperatures remains speculative. Since the pyrolysis reaction is endothermic, heat needs to be supplied to the reactor either by a direct or an indirect manner. A number of different reactors have been reported using different heating methods by various authors and theses are summarised in Table 2.9.

Table 2.9. Review of thermal degradation (cracking) technologies categorized based on the heating method.

Heat carrier loop with external heating	
Technology	Reference
Circulating Fluidized Bed (CFB)	Sodero et al., 1996; Lovett et al., 1997
Bubbling Fluidized Bed (BFB)	Mastellone, 1999
Rotating cone	Westerhout et al., 1997a; Westerhout et al., 1998b; Westerhout et al., 1998c
Spouted bed	Olazar et al., 1992; Aguado et al., 2000; Aguado et al., 2002
Stirred reactor	Masuda et al., 2001
Direct contact or heating with carrier	
Lead bath	Smolders and Baeyens, 2004
Ablative reactor	Rodriguez et al., 2001
Vacuum and plasma reactors	Huang and Tang, 2009

Operating conditions always determine the fate of the reactions obtained. In order to obtain a maximum gas yield, secondary reactions are avoided by operating at high temperatures in a flash pyrolysis process (Ceamanos et al., 2002), whilst reducing residence time and operating temperatures in the pyrolysis process maximises the liquids yield (Williams and Williams, 1997). Reactors used in pyrolysis can be also classified according to the residence time of the solid and gas phase in the reactor: a long residence time of the solids and a short residence time of the gas requires using a bubbling fluidised bed (BFB) reactor, a short residence time for both solid and gas phases is achieved in a core flow CFB reactor (Figure 2.12).

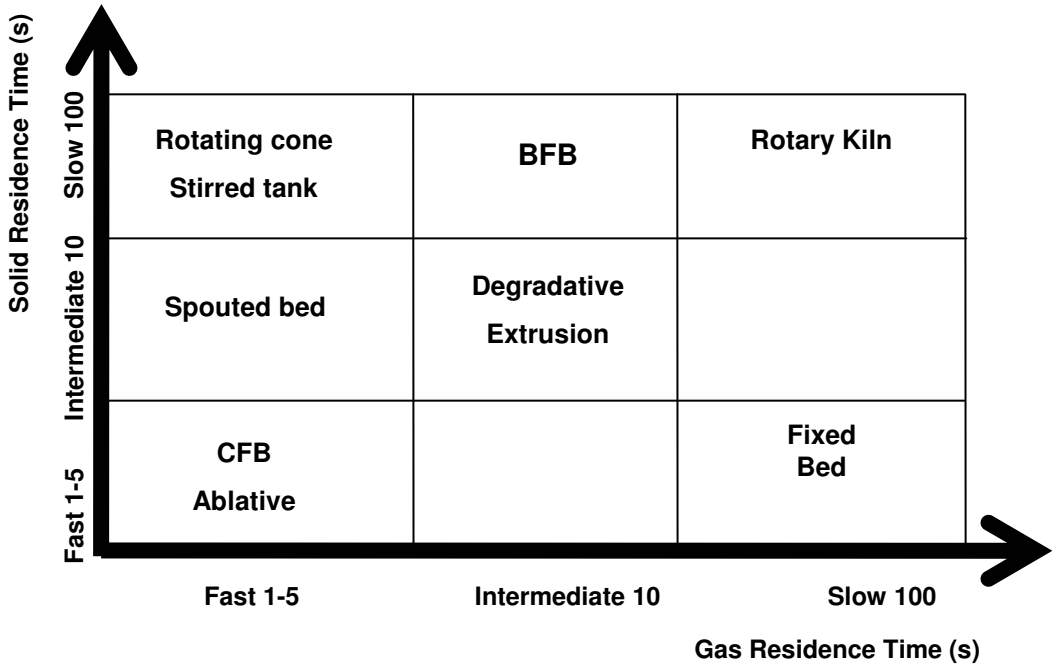

Figure 2.12 - Solid Residence Time (SRT) vs. Gas Residence Time (GRT) for common pyrolysis units.

The kinetics of polymers thermal degradation is studied using either isothermal or dynamic (non-isothermal) methods. Dahiya et al. (2008) stated the advantages and disadvantages of isothermal measurements and the main advantages include: (i) changes in degradation mechanisms are easily detected due to the fact that reaction rates are obtained at a single temperature, hence a change in the order of the reaction can be determined; and (ii) kinetic rates can be obtained by solving analytical equations. However, the main disadvantages are: (i) several experiments are required at different temperatures, therefore varying sample properties; and (ii) the reaction takes place to a certain extent before the sample attains the desired constant temperature.

Dynamic (non-isothermal) methods in a TGA set-up generally involve heating the reactant at a constant heating rate (β) from ambient temperature to one sufficiently high that a transformation occurs. The reaction is considered terminated when the transformation is suppressed or stopped. Dynamic techniques are frequently utilised in the study of reaction kinetics and their popularity is due to the fact that both analytical and kinetic data can be obtained simultaneously from a single experiment and in a relatively short period of time (Agrawal, 1992a). These experiments also provide another advantage, which is the ability to obtain data within a wide range of temperatures and they also provide the opportunity to study the influence of β on the reaction (Oh et al, 2003). Non-isothermal kinetic equations are mathematically more involved, and consequently are not without problems and complexities

(Agrawal, 1992b). The importance of reaction kinetics comes directly from the benefits they provide, in terms of unit operation and design.

The kinetics of chemical reactions depends on the rate determining step (i.e. the slowest step), which in a solid state reaction can be: (i) the nucleation and growth of a product; (ii) diffusion; and (iii) chemical reactions at the interface. However, diffusion problems, heat and mass transfer rates are negligible in TGA pyrolysis studies due to small samples used (typically less than 20 mg) (Conesa et al., 1996; Bockhorn et al., 1999; Ceamanos et al., 2002). From the basic kinetic rate equation, one can derive the expressions for isothermal and dynamic techniques. Dahiya et al. (2008) classed the models of isothermal solid state reactions based on the type of the rate determining step (Table 2.10). Starting with the basic kinetic equation:

$$d\alpha/dt = k\,f(\alpha) \qquad (2.1)$$

where α is the degree of conversion defined as $(m_o\text{-}m)/(m_o\text{-}m_\infty)$, with m_o being the initial mass, m the mass at any time t and m_∞ the final mass; t is the time (s), T is the temperature, k is the temperature-dependant rate constant and $f(\alpha)$ is the function that represent the reaction (*rxn*) model. And this can be often described by degressive kinetics as:

$$d\alpha/dt = k\,(1-\alpha)^n \qquad (2.2)$$

where n is the reaction order and the rate constant k can be expressed using the Arrhenius-type temperature dependence:

$$k = A\exp(-E_a/RT) \qquad (2.3)$$

Hence, Equation (2.2.) becomes:

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n \qquad (2.4)$$

The generalised expression for the dynamic method was also given by Dahiya et al. (2008) as:

$$d\alpha/dT = (A/B)\exp(-E/RT)f(\alpha) \qquad (2.5)$$

where β is the heating rate ($^oC\ min^{-1}$) expressed as dT/dt, E is the apparent activation energy (kJ mol^{-1}), A is the Arrhenius pre-exponential or frequency factor (min^{-1}), sometimes denoted as P

and T is the temperature in K.

There are several methods for deriving kinetic parameters from the previous equation, such as (i) the differential method, i.e. direct application of the equation; (ii) the difference-differential method, i.e. the Freeman and Carroll method; (iii) the integral method using a simple approximation of the exponential temperature integral, i.e. the Coats-Redfern method; and (iv) model-independent methods, i.e. isoconversional methods based on heating rate (such as the Ozawa-Flynn-Wall (OFW) method, the Friedman method or the Kissinger method). Table 2.11 reviews these major methods and states their drawbacks and applications.

Table 2.10 Selected models of isothermal solid state reaction according to Dahiya et al. (2008).

Model Class	Name of model/equations	Differential form, $f(\alpha)$	
Diffusion-controlled models	One dimensional	$1/2\ \alpha$	(2.6)
	Two dimensional	$[-\ln(1-\alpha)]^{-1}$	(2.7)
	Three dimensional – Jander's equation	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	(2.8)
Nucleation and growth controlled models	Avrami-Erofeev's equation, with m = 1.5, 2, 3, 4	$m(1-\alpha)[-\ln(1-\alpha)]^{m-1/m}$	(2.9)
	First order *rxn* (random nucleation)	$1-\alpha$	(2.10)
Contracting phase boundary	Plate (n = 1), cylindrical (n = 2) and spherical (n = 3) geometry	$n(1-\alpha)^{(n-1)/n}$	(2.11)

Table 2.11 Review of the main expressions for the dynamic models used in polymer degradation studies. Source: Dahiya et al. (2008).

Method	Expression(s)	Notes
Differential	$\ln(\frac{d\alpha/dt}{f(\alpha)}) = \ln(A/\beta) - E/RT$; (2.12) Thus, a plot of the left-hand side vs. 1/T yields both E and A from the slope and intercept, respectively. For order-based models, i.e. those involving (1 − a), the reaction order (n) has to be determined by an independent method as such: $1-\alpha_{max} = n^{1/(1-n)}$; (2.13) α_{max} is the fraction reacted at the maximum rate of decomposition.	The suppression of errors due to the logarithmic form of dx_s/dT and need for data filtration smoothing to obtain bias parameters are amongst its major drawbacks.
Freeman and Carroll	$\frac{\Delta\log(d\alpha/dT)}{\Delta\log(1-\alpha)} = \frac{E}{2.3RT}\left[\frac{\Delta(1/T)}{\Delta\log(1-\alpha_s)}\right] + n$; (2.14) where the function withdrawn from the TGA curve is: $f(x_s) = (1-\alpha)^n$ (2.15)	Widely used in literature, but eliminates the evolution of data, and inaccurate in maximum decomposition regions
Integral method	$\log(\alpha) = \log(\frac{AE}{\beta R}) + \log p(x)$ (2.16) $g(\alpha) = \frac{AE}{\beta R} p(x)$ (2.17) $p(x) = \frac{\exp(-x)}{x^2}(1-\frac{2}{x})/(1-m(1/x)^2$; where m = 0 (2.18)	The main controversy is around the p(x) expression were a number of authors have tried to adapt simpler and more representative expressions.
Single heating rate-*Isoconversion OFW* method	$\ln(\beta) + 5.33 + \ln(1-x_s) = \ln(k_o E/R) - 1.05(E/R.T)$ (2.19) Source: Ceamanos et al. (2002)	The major disadvantage is that multi-step process during the course of reaction cannot be detected

2.7. Effect of Operational Conditions, Sample Preparation and Conditioning

Historically, the pyrolysis of polymers has been executed at different scales. TGA has been a widely popular method, especially for determining the reaction kinetics of the studied polymers (Conesa et al., 1996; Ceamanos et al., 2002; Park et al., 2000a; 2000b; Oh, et al., 2003). Previous studies have demonstrated different experimental set-ups used with different inert atmospheres (at different scales), temperature ranges, sample amounts, heating rates (β) and pressures (Conesa et al., 1996; Bilbao et al., 1997; Bockhorn et al., 1998; 1999a; 1999b; Ceamanos et al., 2002; Park et al., 2000a; 2000b; Oh, et al., 2003, Berrueco et al., 2005).

The heat transfer phenomenon (between the experimental system and the sample and inside the sample) is a major issue addressed previously by Ceamanos et al. (2002). This could be minimised by using a small amount of sample and low heating rates. As the pyrolysis temperature increases, the heat demand increases dramatically according to Arrhenius kinetics (knowing that the overall pyrolysis reaction is endothermic). Heat transfer problems across the boundary layer into the reacting solid surface (substrate) become acute at high heating rates. This was also detailed by Narayan and Antal (1996) who addressed the thermal lag (ΔT_{TL}) problem between the sample's temperature and the temperature of the sample's environment achieved by placing an external thermocouple onto the sample. The difference between these two temperatures is what they have defined as the thermal lag (ΔT_{TL}).

There are great variations in the calculated kinetic parameters (namely the kinetic rate constants and activation energy), depending on the approach and the analytical method used (Oh et al., 2003). Consequently, the adequacy of the kinetic model assumed for the complex degradation mechanism is very important (Ceamanos et al. 2002). Differences due to the reaction mechanisms and kinetic evaluation methods have been reported in the past by various authors (Conesa et al., 1996; Bilbao et al., 1997; Bockhorn et al., 1998; 1999a; Ceamanos et al., 2002; Park et al., 2000a; 2000b; Oh, et al., 2003). Conesa et al. (1996) showed that the initial weight of the sample and the surface pan area can affect the displacement of the weight loss curve. Ranzi et al. (1997) stressed the possible presence of mass and heat transfer limitations, generally not taken into account in kinetic data abstraction, which extend the range of variation of kinetics constants. Whilst Dahiya et al. (2008) stated that small errors in temperatures and heating rates cause notable deviations in kinetic parameters. In summary, operating conditions can affect significantly the results obtained by any experimental pyrolysis set-up. Some of the issues illustrated here are addressed in Chapters 3 and 4.

2.8. Modelling & Reaction Mechanism Schemes

Understanding the thermal chemistry of hydrocarbons is essential in a number of processes, these include: (i) petroleum, coal and biomass conversion to liquid fuels; (ii) the cracking of higher hydrocarbons to produce light olefins; (iii) the degradation of endothermic jet fuels; and (iv) the depolymerisation and recycling of synthetic polymers (Savage, 2000). This section reviews the degradation mechanism of PE in pyrolysis. The kinetic modelling work carried out in this thesis focuses on the development of a reaction mechanism model for the pyrolysis of PE. Consequently, previous studies focusing on the development of reaction mechanisms are reviewed in this section.

The thermal degradation of polymers is a molecular deterioration process that occurs due to overheating, in which the long backbone chain of a polymer starts to separate (i.e. molecular scission) and react with another to change the properties of a polymer (ZEUS, 2005). In the case of PE pyrolysis, the depolymerisation mechanism involves several steps: initiation, free radical transfer (or propagation) and termination (Simha et al., 1958; Conesa et al., 1996; Horvat and Ng, 1999). Random chain scission, end chain scission, chain stripping, cross linking and coke formation are all types of reactions that a polymer undergoes when subjected to a heating condition (Oh et al., 2003). Bockhorn et al. (1999a) have illustrated their radical chain mechanism in a comprehensive way, as shown in Figure 2.13. The mechanism is initiated by a random scission of the polymer chain into primary radicals (R_p), β-scission then leads to the formation of ethene (C_2H_4) which is a by product that forms in the temperature range (430 – 480°C), as stated by Bockhorn et al. (1999a).

At lower temperatures, the formation of stable radicals (R_s) occurs due to intramolecular transfer. Subsequent β-scission of the secondary radicals contributes to the radical chain mechanism because the primary radical is produced in each step (propagation). Two β-scission reactions are possible: one leads to alkenes, whereas the other leads to the formation of a short primary radical and a polymer with a terminated double bond. The termination of the reaction is assumed via a combination reaction of the primary radicals. Further details of the mechanism can be found elsewhere (Bockhorn et al., 1999a; Ceamanos et al., 2002; ZEUS, 2005). One of the main aspects of the thermal decomposition of PE is that it melts at temperatures around 120°C before it decomposes (Conesa et al., 1996). However, previous reports claim that PE has been found stable up to 290°C, with appreciable product formation at temperatures around 370°C (Oakes and Richards, 1949). A number of reaction schemes for the pyrolysis of PE have been developed over the years and these are summarised in Table 2.12 alongside models found in the literature that are relevant to PE pyrolysis.

Initiation:

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2 \sim \xrightarrow{k_1} \sim CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2 + {}^{\bullet}CH_2\text{-}CH_2\text{-}CH_2 \sim$$

P **$2R_P$**

Propagation:

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2 \xrightarrow{k_2} \sim CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2 + CH_2 = CH_2$$

R_P **R_P**

Intramolecular hydrogen transfer:

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}{}^{\bullet}CH_2 \xrightarrow{k_3} \sim CH_2\text{-}CH_2\text{-}{}^{\bullet}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

R_P **R_S**

β-Scission:

$$\sim CH_2 - CH_2 - {}^{\bullet}CH - CH_2 - CH_2 - CH_2 - CH_3 \longrightarrow \begin{cases} \xrightarrow{k_4} \sim CH_2^{\bullet} + CH_2 = CH - CH_2 - CH_2 - CH_2 - CH_3 \\ \xrightarrow{k_4'} \sim CH_2 - CH_2 - CH = CH_2 + {}^{\bullet}CH_2 - CH_2 - CH_3 \end{cases}$$

R_S **R_P** **Alkene/dienes** **P** **R_P**

Intermolecular hydrogen transfer:

$$CH_3 - (CH_2)_n - CH_2 - {}^{\bullet}CH_2 + \sim CH_2 - CH_2 - CH_2 \sim \xrightarrow{k_5} CH_3 - (CH_2)_n - CH_2 - CH_3 + \sim CH_2 - {}^{\bullet}CH - CH_2 \sim$$

R_P **Alkene** **R_S**

Termination:

$$\sim {}^{\bullet}CH_2 + \sim {}^{\bullet}CH_2 \xrightarrow{k_6} \sim CH_2 - CH_2 \sim$$

$2R_P$ **P**

Figure 2.13 - Radical chain mechanism of thermal degradation of polyethylene (PE). Source: Bockhorn et al. (1999a).

Table 2.12 Summary of reaction schemes/models and the main mathematical breakdown of previous authors investigating polyethylene pyrolysis.

Reference	Model/scheme	Main mathematical breakdown	Main findings
Conesa et al.(1994)- Three reaction scheme	$P \xrightarrow{k_1} aG_1 + bA_1$ (2.20) $P \xrightarrow{k_2} P^* \xrightarrow{k_3} a'G_2 + b'A_2$ (2.21)	$M_o\, dP/dt = -k_1 S(\frac{P}{P+P^*}) - k_2 P M_o$ (2.22) $M_o\, dP^*/dt = k_2 P M_o - k_3 S(\frac{P}{P+P^*})$ (2.23) $dPE/dt = k_1(S/M_o)(\frac{P}{P+P^*}) - k_3(S/M_o)(\frac{P^*}{P+P^*})$ (2.24)	The kinetic rate constants were taken as a variable depending on the Arrhenius equation: $k_i = k_{io}\exp(-E_i/RT)$: i = 1, 2, 3 (2.25) And the results could be summarized as follows: k_{01} = 2.892 x 10^{19} s^{-1} m^{-2} kg^{-1}, E_1 = 171.1 kJ mol^{-1} k_{02} = 2.830 x 10^{13} s^{-1}, E_2 = 234.6 kJ mol^{-1} k_{03} = 2.349 x 10^{20} s^{-1} m^{-2} kg^{-1}, E_3 = 195.8 kJ mol^{-1}
Conesa et al.(1994)- Zero kinetic	$PE \xrightarrow{k_1} aGp + bAp$ (2.26)	$-dPE/dt = k_1(S/M_o)$ (2.27)	The kinetic rate constant was found equal to 8.5 x 10^{18} s^{-1} m^{-2} kg^{-1} and activation energy was found 164.3 kJ mol^{-1}.
Conesa et al. (1996)	$P \xrightarrow{k_1} G_1$ (2.28) $P \xrightarrow{k_2} P^* \xrightarrow{k_3} G_2$ (2.29)	$dP/dt = -k_1(S/m_o)(\frac{P}{P+P^*}) - k_2 P$ (2.30) $dP^*/dt = k_2 P - k_3(S/m_o)(\frac{P}{P+P^*})$ (2.31)	Results in dynamic runs: k_1 = 4.852 x 10^9 kg s^{-1} m^{-2} (E_1 = 1885 kJ mol^{-1}) k_2 = 2.670 x 10^{15} s^{-1} (E_2 = 271.1 kJ mol^{-1}) k_3 = 2.319 x 10^{11} kg s^{-1} m^{-2} (E_3 = 221.5 kJ mol^{-1}) Results in isotehrmal runs: k_1 = 4.730 x 10^{10} kg s^{-1} m^{-2} (E_1 = 214.2 kJ mol^{-1}) k_2 = 1.600 x 10^{14} s^{-1} (E_2 = 238.9 kJ mol^{-1}) k_3 = 1.600 x 10^{11} kg s^{-1} m^{-2} (E_3 = 200.0 kJ mol^{-1})
Horvat and Ng (1999); McCaffrey et al., (1995)	Assuming that the polymer thermolysis occurs via a random chain scission and the molecules in the reactor reach a minimum chain length for evaporation.	Atkinson and Maccallum (1971) model : $W(t) = \frac{W_o[(a+1)\exp(k_s.t) - a.\frac{P_o - a - 1}{P_o - a}][P_o - a]}{P_o\exp((a+1)k_s t)}$ (2.32) : P_o is the initial degree of polymerization	The experiments were conducted in a semi-batch reactor, with an initial charge of 15 g and the following rate constants were estimated: k_s(at 410°C) = 1.24 x 10^{-4} min^{-1} k_s(at 420°C) = 2.49 x 10^{-4} min^{-1} k_s(at 440°C) = 1.00 x 10^{-3} min^{-1}

In conclusion, several authors have developed reaction mechanism schemes for the pyrolysis depolymerisation of PE (Conesa et al., 1994; 1996; McCaffrey et al., 1995; Horvat and Ng, 1999; Ceamanos et al., 2002). The reaction chemistry of PE depolymerisation was reported by Bockhorn et al. (1999a) and can be summarised as follows:

- Initiation step: whereby the mechanism is initiated by a random chain scission of the polymer chain producing primary radicals (R_p).
- Propagation: where stable radicals (Rs) are produced due to intramolecular transfer. Two possible β-scissions reactions are then possible. One leads to alkenes, whereas the other leads to the formation of a short R_p and a polymer with a terminated double bond.
- Termination: assumed to be via combination, which leads to a residual polymer.

Conesa et al. (1996) have stated that PE melts at a temperature around 120°C before it starts to decompose. In this thesis, an intermediate stage of PE (a molten state) has been considered producing waxes in the development of the reaction mechanism model (see Chapters 3 and 4). Considering an intermediate state was also reported in earlier studies of pyrolysis by Conesa et al. (1996) and Ceamanos et al. (2002).

2.9. Micro Scale Studies in Thermogravimetric (TG) Fixed Bed Set-ups

Pyrolysis produces three different phases: a solid phase (char, 5-25 wt %), a liquid phase (tars, 10-45 wt %) and a gas phase (Aznar et al., 2006, Zia et al., 2007). The first products yielded are usually in the range of C_{20} to C_{50}. These products are cracked in the gas phase to obtain lighter hydrocarbons, as ethene (ethylene) and propene (propylene), which are unstable at high temperatures and react to form aromatic compounds such as benzene or toluene. If the residence time is long, then coke, methane and hydrogen will form (Westerhout et al., 1998a).

In the TCT of polyolefins (mainly PE and PP), the products obtained depend mainly on the cracking reactions in the gas phase. Long residence times of volatiles in the reactor and high temperatures lead to a decrease in tar production but an increase in char formation (Cozzani et al., 1997). The main disadvantage of plastic pyrolysis is that it is necessary to control the chloride content (when present) in the feedstock and the risk of mal-fluidisation because of particle agglomeration (Kaminsky et al., 1995). It is believed that increasing the temperature to above 500°C and prolonging the gas residence time will result in a reduction of the tar content in the gas product from both pyrolysis and gasification of PSW, ASR, MSW and even mixtures of coal, biomass and PSW (Stiles and Kandiyoti, 1989; Pinto et al., 2003; Zolezzi et al., 2004;

Miscolczi et al., 2004; Ciliz et al., 2004). At temperatures above 800°C, larger paraffins and olefins produced from the decomposition of plastics are cracked into H_2, CO, CO_2, CH_4 and lighter hydrocarbons (Ponzio et al., 2006). As a result of methyl-group abstraction from aromatics and decomposition of paraffins, C_2H_4 and C_2H_2 are typically reported to increase with temperature (Ledesma et al., 2000). The abstraction of methyl groups and hydroxyl groups from aromatic structures implies that the aromatic fraction does increase with temperature even though the total amount of tar decreases. H_2-abstraction from light hydrocarbons and cross-linking reactions may also produce poly-aromatic hydrocarbons (PAH).

Kinetic data obtained by previous authors confirms that different molecular structures lead to different mechanisms of decomposition and rates (Bockhorn et al., 1999b). Table 2.13 reviews some of the major studies in the literature reporting on the apparent activation energy (E_a) and overall kinetic rate constant (k_o) obtained from the pyrolysis of polymers under isothermal and dynamic conditions.

Table 2.13 Survey of apparent activation energy (E_a) and pre-exponential factor (k_o) studies found in literature with emphasis on major polymers.

Polymer	Notes	E_a (kJ mol^{-1})	Rate Constant (k_o)[4]	n	Reference
Polyethylene (PE)					
Synthesized Bakelite Corp PE	In TG dynamic conditions (246-480^{o}C)[1,2]	Freeman & Carroll method			Anderson and Freeman (1961)
	ζ (wt%) = (m_o-m)/m) = < 3	201	-	0	
	ζ (wt%) = (m_o-m)/m) = 3 – 15	255	-	0 -1	
PE	200 – 600 ^{o}C	259	7.2 x 10^{13} s^{-1}	0.81	Westerhout et al. (1997b)[3]
BASF Corp Polymers	In TG dynamic conditions				
HDPE	387-467 ^{o}C	247-330	-	0 -1	Mucha (1976)
LDPE	387-467 ^{o}C	163-230	-	0 -1	Mucha (1976)
	In TG dynamic conditions (β = 5-10 ^{o}C min^{-1})				
HDPE	400-485 ^{o}C	304[1]	1.3 x 10^{21} s^{-1}	1	Urzendowski and Guenther
	410-485 ^{o}C	320	7.1 x 10^{21} s^{-1}	1	(1971)
LDPE	375-480 ^{o}C	290[1]	3.1 x 10^{20} s^{-1}	1	
	380-485 ^{o}C	303	5.8 x 10^{21} s^{-1}	1	
Commercial grade USIFE HDPE	In TG dynamic conditions (β = 1, 2, 5.5 K min^{-1})				
Commercial grade USIFE LDPE		234	9.3 x 10^{13} s^{-1}	0.74	Wu et al. (1993)
	327-487 ^{o}C	206	1.2 x 10^{12} s^{-1}	0.63	Wu et al. (1993)
	327-487 ^{o}C				
	In TG isothermal conditions	220	1.9 x 10^{13} s^{-1}	1	
HDPE	400-450 ^{o}C	241	1.0 x 10^{15} s^{-1}	1	Westerhout et al. (1997b)
LDPE (grade 1)	400-450 ^{o}C	201	9.8 x 10^{11} s^{-1}	1	
LDPE (grade 2)	400-450 ^{o}C				
Polypropylene (PP)					
IPP	Temperature range: 380-435^{o}C	213	-	-	Dickens (1982)

Table 2.13 (Cont'd) Survey of apparent activation energy (E_a) and pre-exponential factor (k_o) studies found in literature with emphasis on major polymers.

Polymer	Notes	E_a (kJ mol^{-1})	Rate Constant (k_o)[4]	n	Reference
BASF Corp PP (no additives)	Isothermal set-up	220±5	log (k_o) =15.06±0.06 min^{-1}	1.1	Bockhorn et al. (1998)
BASF Corp PP (no additives)	Dynamic set-up	223.7±1.6	log (k_o) = 15.90±0.02 min^{-1}	0.77	Bockhorn et al. (1998)
PP fibres (Argon environnement)	In TG dynamic conditions (β = 5, 10, 15, 20 K min^{-1})		-	-	Gambiroza-Jukic and Cunko (1992)
	ζ (wt%) = (m_o-m)/m) = 5-90	83-128	-	-	
	ζ (wt%) = (m_o-m)/m) = 9-53	99	-	-	
	ζ (wt%) = (m_o-m)/m) = 10-50	99			
FU-CHU PP			6.3 x 10^{10} s^{-1}	0.90	Wu et al. (1993)
	In TG dynamic conditions (β = 1, 2, 5.5 K min^{-1})	184			Westerhout et al. (1997b)
PP Grade 1	In TG isothermal conditions		3.2 x 10^{15} s^{-1}	1	
PP Grade 2	400-440°C	244	2.2 x 10^{11} s^{-1}	1	
	400-440°C	188			
Polystyrene (PS)					
PS	TG Isothermal set-up	172±4	log (k_o) =12.47±0.02 min^{-1}	1.04	Knümann and Bockhorn (1994)
PS	TG Dynamic set-up	322.8±2.4	log (k_o) =24.61±0.19 min^{-1}	1.09	Knümann and Bockhorn (1994)
Koppers Corp PS	In TG dynamic conditions (246-430°C)[1,2]				
	ζ (wt%) = 0-10	193	-	0	Anderson and Freeman (1961)
	ζ (wt%) = 15-95	231-273	-	1	
CHI-MEI PS	In TG dynamic conditions (β = 1, 2, 5.5 K min^{-1})		5.0 x 10^{10} s^{-1}	0.5	
PS	500-800°C	92			
	In TG isothermal conditions		-	1	Wu et al. (1993)
PS	365-400°C	204			
			3.3 x 10^{13} s^{-1}	1	Mertens et al. (1982)
					Westerhout et al. (1997b)
Polyethylene terephthalate (PET)					
BASF Corp PET (no additives)	Isothermal	214 ± 2	log (k_o) = 15.20±0.04 min^{-1}	1.15	Bockhorn et al. (1998)
BASF Corp PET (no additives)	Dynamic	238.7	log (k_o) = 18.00 min^{-1}	1.15	Bockhorn et al. (1998)

Table 2.13 (Cont'd) Survey of apparent activation energy (E_a) and pre-exponential factor (k_o) studies found in literature with emphasis on major polymers.

Polymer	Notes	E_a (kJ mol^{-1})	Rate Constant (k_o)[4]	*n*	Reference
PET (Source 1)	In TG dynamic conditions (β = 10, 15, 25 K min^{-1})	ASTM E698[5] method (162.15)	ln(k_o) = 26.37 min^{-1}	1	Saha and Ghoshal (2005)
PET (Source 2)	In TG dynamic conditions (β = 10, 15, 25 K min^{-1})	ASTM E698[5] method (162.15)	ln(k_o) = 34.81 min^{-1}	1	Saha and Ghoshal (2005)

[1] Vacuum environment
[2] Possible heat and mass limitations during experimentation
[3] Taken from the cited. *Original reference in German*.
[4] Expressions reporting log(k_o) are derived from the following: $d\alpha/dt = k_o \exp(-E/RT).(1-\alpha)^n$

2.10. End of Life Tyres (ELTs): Thermo-Chemical Studies & Utilization

Whereas the review of pyrolysis reported in the previous sections focused on polymer materials, here the focus is on end of life tyres (ELTs). A number of studies carried out in thermogravimetric systems show that ELTs start to thermally degrade at approximately 200°C and totally degrade at around 500°C (Berrueco et al., 2005). Previous reports of inert or partially oxidised atmosphere treatment tend to concentrate on intensifying the gas yield of the resultant products, and these are summarised in Table 2.14.

Conesa and Font (1999) introduced the kinetic severity function (KSF) as a validation for their kinetic models (forming (n-pentane) C_5). If a paraffin is designated by the subscript i (its number of carbons) and uses the subscript 5 to designate n-pentane, then the exponential form of the Arrhenius equation can be expressed as:

$$k_i = A_i.\exp(-E/RT); k_5 = A_5.\exp(-E_5/RT); \\ k_f/k_5 = (A_f/A_5).\exp(-E + E_5/RT) \tag{2.33}$$

The yields of the products obtained from a pyrolysis process are due to the decomposition of the raw material (primary reactions) and to the reactions the primary volatiles undergo (secondary reactions). The KSF was then defined by the following equation:

$$KSF = \int_0^{\tau} k_5.dt \\ : T = Const. \Rightarrow KSF = k_5.\tau \tag{2.34}$$

where τ is the total time. The KSF is very useful both for correlating yield data and for designing and evaluating the performance of cracking coils. The most obvious advantage is that it recognizes and incorporates both time and temperature in such a way that it is consistent with kinetics. Such a methodology was primarily used for the thermal cracking of ELTs in Conesa et al. (2000) (see Table 2.14).

Table 2.14 Summary of previous studies on ELTs pyrolysis in inert, sub-stoichiometric and pure oxygen atmosphere.

Reference	Temperature range (°C)	Main products (%)	*Comments*
Conesa et al. (2000)	600-800	Gases 6-37	Three reactors were used, (sand) FBR, Pyroprobe pyrolyser and two horizontal quartz reactors. Very minimal liquid and char yield in a Fluidized bed reactor. The primary reaction was considered as follows: $\mathrm{ELTs} \xrightarrow{\text{PrimaryPyrolysis}} \mathrm{aG_p} + \mathrm{bA_p}$ (2.35) $\mathrm{bA_p} \xrightarrow{k_{s1}} \mathrm{Gs} + \mathrm{Ss}$ Where p and s stand for primary and secondary products.
Williams et al. (1990)	300-720	55 (Oil) 10 (Gas) 35 (Char)	Experiments carried out in a static batch reactor with N_2 jacket.
Cunliffe and Williams (1999)	450-600	Gases 5-9	Experiments carried out in a static batch reactor with N_2 jacket.
Bouvier et al. (1987)	327–525	39 (Oil) 6 (Gas) 38 (Char)	Externally heated retort reactor was used.
Lucchesi and Maschio (1983)	400–700	38-49 wt% converted into oil	Pyrolysis in a bench scale moving bed. The gas product contained mainly CH_4, H_2, CO, CO_2 and light hydrocarbons.
Wu et al. (1997)	400-500	30% carbon black	Fluidized Bed Reactor (FBR) pyrolysis

Chen et al. (2001) investigated the pyrolysis of two tyre grades (passenger and truck) thermogravimetrically under a β of 5, 10, 20 and 30 K min^{-1} and a temperature range of 373-1273 K. The initial reaction temperatures were 482-521 K for the tyre of the passenger car and 458–511 K for the truck tyre. Both ELTs exhibited similar behaviours, which was as the initial reaction temperature decreased, both the reaction range and reaction rate increased when the heating rate increased. The overall rate equation for each tyre can be modelled satisfactorily by a simple equation from which the kinetic parameters, such as the activation energy (E), the pre-exponential factor (A), and the reaction order (n) of unreacted material based on the Arrhenius form can be determined using Friedman's method.

The following reaction was assumed:

$$\text{ELTs} \xrightarrow{k} \text{volatiles} \tag{2.36}$$

Further, the rate equation of conversion factor α is expressed in Arrhenius relation in the form of

$$\frac{d\alpha}{dt} = A.\exp(-E/RT).f(\alpha)$$
$$:\alpha = (W_o - W)/(W_o - W_f) \tag{2.37}$$

where t is the time (min), A the pre-exponential factor (min^{-1}), E the activation energy (kJ/mol), T the reaction temperature (K), R the universal gas constant, W (mg) the mass of the sample at time t, and W_0 (mg) and W_f (mg) are the initial and final (or residual) mass of the sample, respectively. The results show that the two ELTs behaved similarly and the average kinetic parameters of the two tyres were E =147.95± 0.21 kJ/mol, A = (6.295±1.275) × 10^{10} min^{-1}, and n = 1.81±0.18. The predicted rate equations compare well with the measured data (Chen et al., 2001).

Laresgoiti et al. (2000) published their results on the pyrolysis of ELTs. Representative samples of a whole car tyre were pyrolysed under nitrogen in a 3.5 dm^3 autoclave at 400, 500, 600 and 700°C. Tyre pyrolysis gases were composed of CO, CO_2, H_2S, and hydrocarbons such as CH_4, C_2H_4, C_3H_6, C_4H8, etc. and the unsaturated derivatives. Multidimensional gas chromatography using three capillary columns installed in a sole furnace were used together with a thermal conductivity detector (TCD) and flame ionisation detector (FID) which were both connected on-line. At higher temperatures, more CO_x ($CO+CO_2$) was produced, which was derived from inorganic components. Leung and Wang (1998) investigated the kinetics of the pyrolysis and combustion of scrap tyres using thermogravimetric and derivative TGA methods. Three materials, namely tyre rubber powder, tyre fibre and wood powder were studied. The reaction

considered was as follows:

$$\mathrm{ELT} \longrightarrow \mathrm{Medium(1)} \xrightarrow{k1} \mathrm{Medium(2)} \xrightarrow{k2} \mathrm{Char} \qquad (2.38)$$

The reaction was mathematically expressed as follows:

$$\ln[\frac{d\alpha}{dt}] = \ln\sum_{i=1}^{n} d\alpha_i/dt = \ln\sum_{i=1}^{n} A.\exp(-E/RT).(1-\alpha) \qquad (2.39)$$

It was found that the process and kinetic parameters varied with heating rates but were less dependent on the powder sizes. The simulations by the proposed models agreed well with the experimental data.

In conclusion, various authors have reported on the pyrolysis of ELTs in a number of experimental set-ups and on different scales (Lucchesi and Maschio, 1983; Bouvier et al., 1987; Williams et al., 1990; Wu et al., 1997; Cunliffe and Williams, 1999; Conesa et al., 2000; Chen et al., 2001). Gases, oil and char are the primary products found after the termination of the reaction, and gases and char are typically included in the development of the reaction mechanisms. In the studies published previously by Laresgoiti et al. (2000) and Chen et al. (2001), volatiles or medium stages of products were assumed, however no lumped product models have been developed in the past to include all the products yielded. This approach is developed and presented in this thesis *(see Chapters 3 & 4)*.

Chapter 3

On the Isothermal Pyrolysis of Different Polymer Grades of Virgin and Recyclate Polyolefins

The objective of this chapter is threefold: to present the results from an investigation into the isothermal reaction kinetics associated with polymers thermal cracking; to assess the thermal behaviour of the materials under the same isothermal conditions; and to illustrate a novel model developed on the basis of product groups as yielded by pyrolysis.

Over the past seventy odd years, the plastics industry has witnessed a drastic growth, namely in the production of synthetic polymers represented by polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl alcohol (PVA) and polyvinyl chloride (PVC). In particular, PE has been a target for product conversion, lubricant production and chemicals recovery. This chapter covers the pyrolysis of two virgin grades of high density polyethylene (HDPE), virgin low density polyethylene (LDPE) and two recycled grades of medium density polyethylene (MDPE) using thermogravimetric analysis (TGA) at high heating rates and pre-set temperatures, similar to industrial fast pyrolysis units. TGA is especially suitable given that the gas residence time is very short, thus limiting undesirable side-reactions. Experiments were carried out in the range of 500-600^{o}C. The data obtained enabled the assessment of the degradation mechanism of the different polymers investigated, on the basis of lumped products, i.e. gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), aromatics (single ring structures) and waxes (> C_{11}). The model developed predicts the pyrolysis yield of the four different products and the polymer residual fraction at any operating condition proving to be a useful tool for reactor design and simulation.

Parts of this chapter were published in:

Lettieri, P. and Al-Salem, S.M., (**2011**). Thermo-Chemical Treatment of Plastic Solid Waste, Chapter in 'Handbook of Waste Management and Recycling', Edited by: Trevor Letcher; Daniel Vallero, Elsevier, ISBN: 978-0-12381-475-3.

Al-Salem, S.M. and Lettieri, P., (**2010**). Kinetic study of high density polyethylene (HDPE) pyrolysis, *Chemical Engineering Research & Design*, **88(12)**; 1599-1606.

3.1. Experimental & Methodology

3.1.1. Materials and Experimental Set-up

Thermogravimetric analysis (TGA) was performed on the polymers tested. Thermogravimetry is a thermal process used to determine changes in weight as a function of temperature in a controlled atmosphere. Three virgin polymers and two recyclate grades were tested and physical properties (melting temperature and particle density) are reported in Table 3.1. The experiments were conducted by Ravago Plastics Co. (Belgium) and weight fractions of polymer (x_p) as a function of time (s), as well as the final collected weight fractions of lumped products (waxes (x_w), gases (x_g), liquids (x_l) and aromatics (x_a) were provided by the company. The reported polymer and products final fractions are the averaged value of the experiments repeated three times by the company. The TGA was conducted using a Universal V3.7A model thermobalance (fixed bed) reactor (Figure 3.1). Product analysis was carried out using a Hewlett Packard 6890 chromatograph provided with thermal conductivity (TCD) and flame ionization (FID) detectors, being connected online to the balance by means of a thermostated line. Furthermore, lump product identification was carried out by means of a mass spectrometer (Shimadzu GCMS-QP20 I OS). Polymer pellets were milled to a size below 0.1 mm (in diameter), and a sample of 15 mg in weight was used in each individual TGA run to avoid heat and mass transfer problems. Pyrolysis products were lumped into gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}) and waxes (> C_{11}).

Table 3.1. Virgin and recyclate grades of polymers used in the isothermal pyrolysis experiments.

Polymer	T_m (°C)	Particle Density ρ (g cc^{-1})[1]	Notes
High Density Polyethylene (HDPE no.1)	133	-	Commercial grade
High Density Polyethylene (HDPE no.2)	131	0.952	Extrusion resin grade
Low Density Polyethylene (LDPE)	109	0.920	Film grade
Medium Density Polyethylene (RMDPE no.1)	-	0.9445[1]	3x3 mm granules
Medium Density Polyethylene (RMDPE no.2)	-	0.9361[1]	3x3 mm granules

[1] Density determined via gradient column test at the time of sample delivery in accordance with ASTM D-1505-96 (1990).

3.1.2. Polymer Loss & Product Formation Patterns

Figures 3.2-3.16 show the polymer weight loss for HDPE nos.1 and 2, the LDPE and the MDPE nos.1 and 2. Analysis of the reaction time and the polymer weight loss aids the understanding of the behaviour exhibited by each polymer grade investigated. With regards to the virgin grades (HDPE nos.1, 2 and LDPE), at 500°C the HDPE no.1 experiment terminated at 510 s (Figure 3.2), whilst HDPE no.2 and LDPE terminated at 600 s (Figures 3.5 and 3.8). A TGA experiment terminates when there is complete loss of the polymer within the crucible (sample holder). This can be better observed during isothermal experiments rather than in dynamic set-ups, where residual polymer material was witnessed when commercial grades were used rather than pure chemicals. Isothermal runs are time dependent; hence, a run terminated when the total degradation of the polymer was achieved.

LDPE showed a similar weight loss pattern to HDPE no.2 (Figures 3.5 and 3.8). At 500°C, LDPE exhibited a slightly quicker polymer loss ($x_p = 0.7$) than HDPE no.2 ($x_p = 0.73$) after 20 s of reaction time. At 550°C, LDPE lost over half its initial sample weight after 20 s of the experiment ($x_p = 0.21$). There were no noticeable differences between the two recyclate grades of MDPE in terms of polymer loss (Figures 3.11-3.16). The melting point (T_m) of the LDPE tested is lower than the other two virgin HDPE grades (see Table 3.1), and this may explain why the polymer degraded slightly quicker than the other virgin grades and may also explain the variation in product formation.

At 550°C, a rapid decrease in the polymer fraction was witnessed with the virgin grades (Figures 3.3, 3.6, 3.9). The typical shape of an S-curve was witnessed to quickly shrivel and decay. The time it took to record the last sample varied between the virgin grades, ranging from 91 s in the case of HDPE no.1 to 200 s for LDPE. The higher the isothermal experimental temperature, the faster it took to reach full degradation. This has also been reported previously by many authors (Westerhout et al., 1997b; Ceamanos et al., 2002; Mastral et al., 2002).

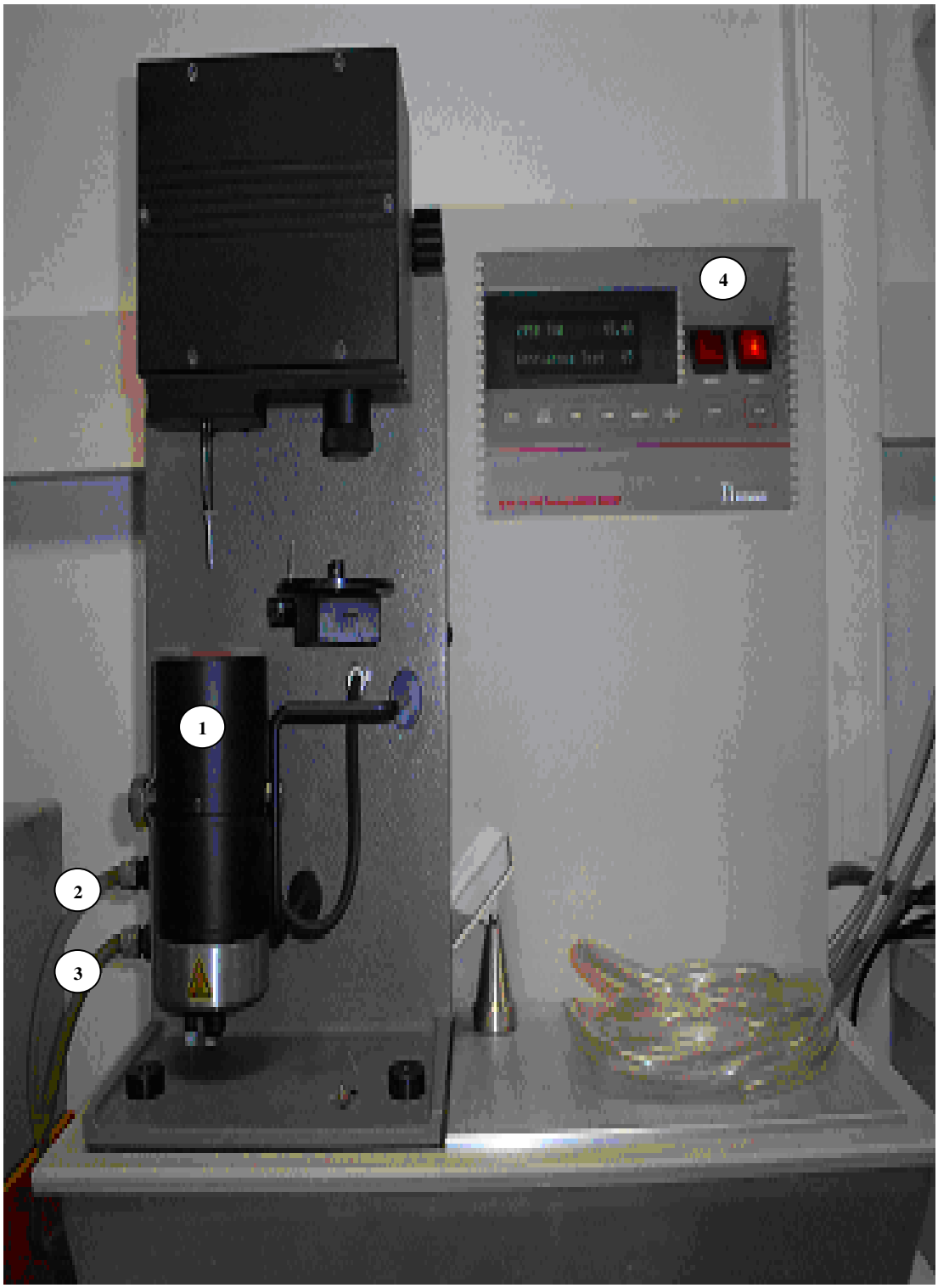

Figure 3.1 - TGA set-up used in the pyrolysis experiments (Ravago Plastics Co, Belgium).
Key: 1. Heating chamber; 2. N_2 inlet; 3. Air inlet; 4. Control display.

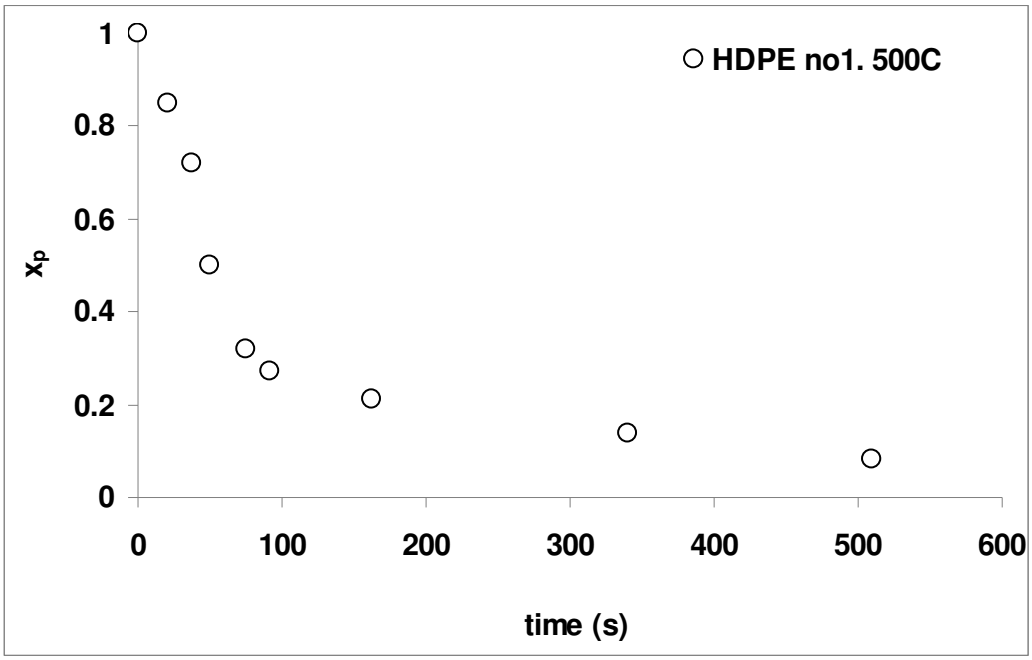

Figure 3.2 - Experimental data (HDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 500°C.

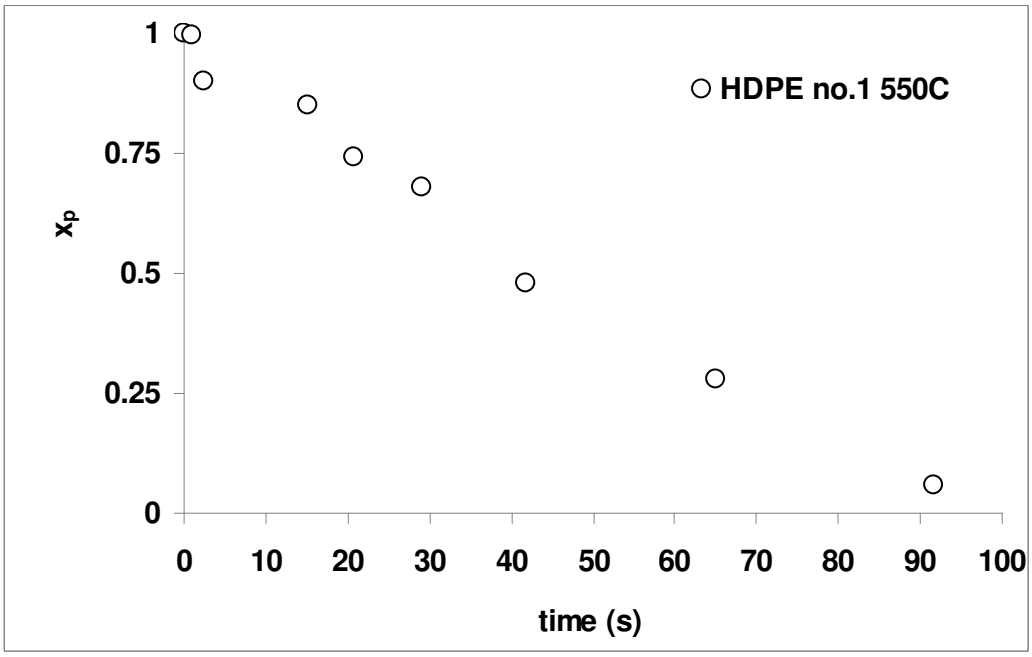

Figure 3.3 - Experimental data (HDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 550°C.

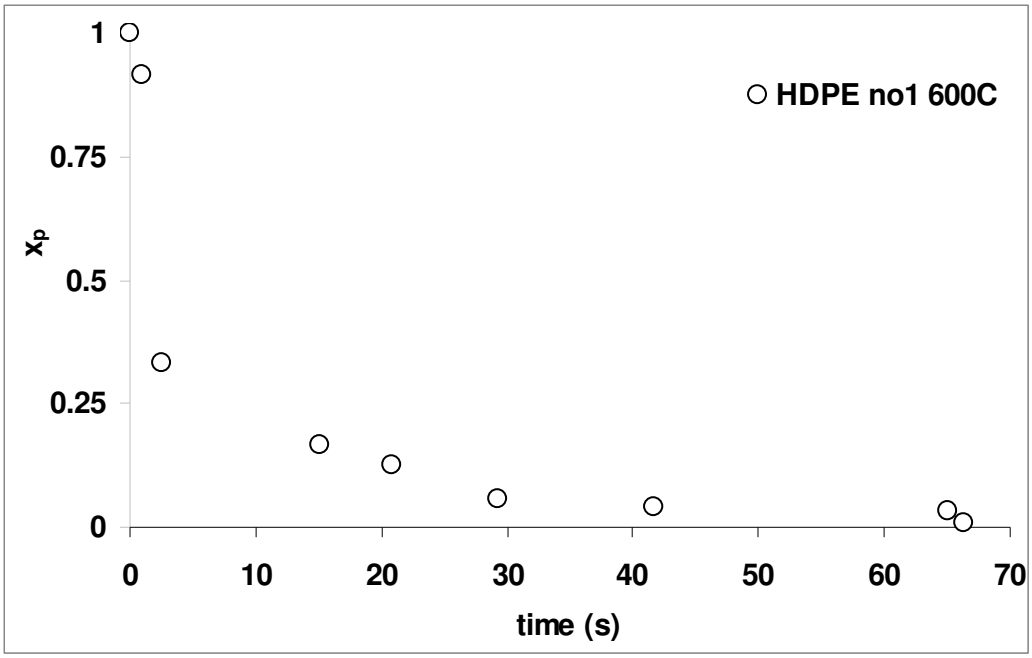

Figure 3.4 - Experimental data (HDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 600°C.

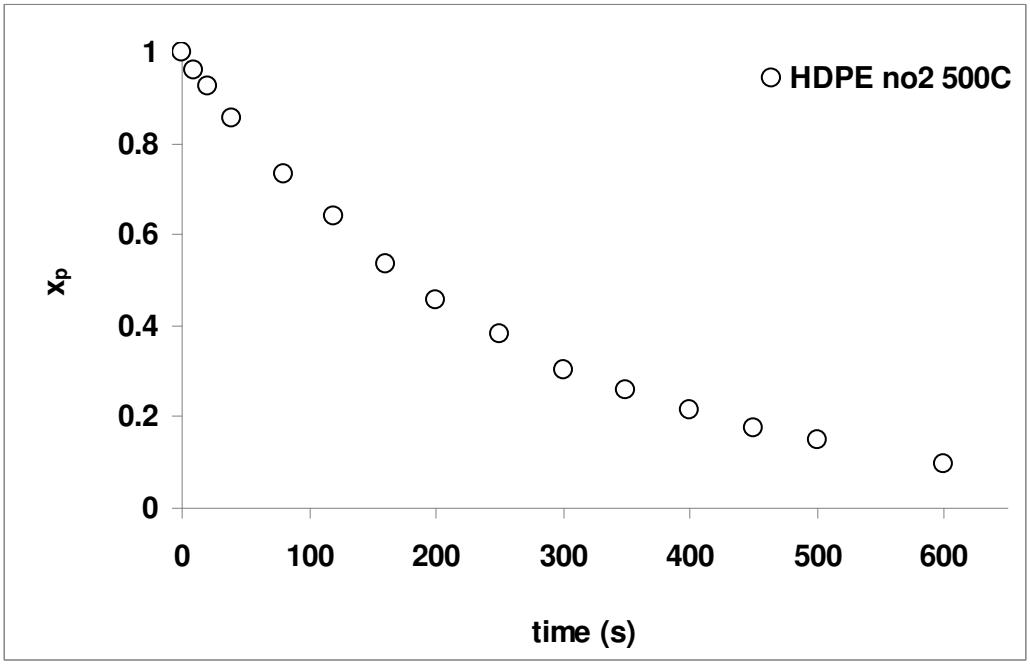

Figure 3.5 - Experimental data (HDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 500°C.

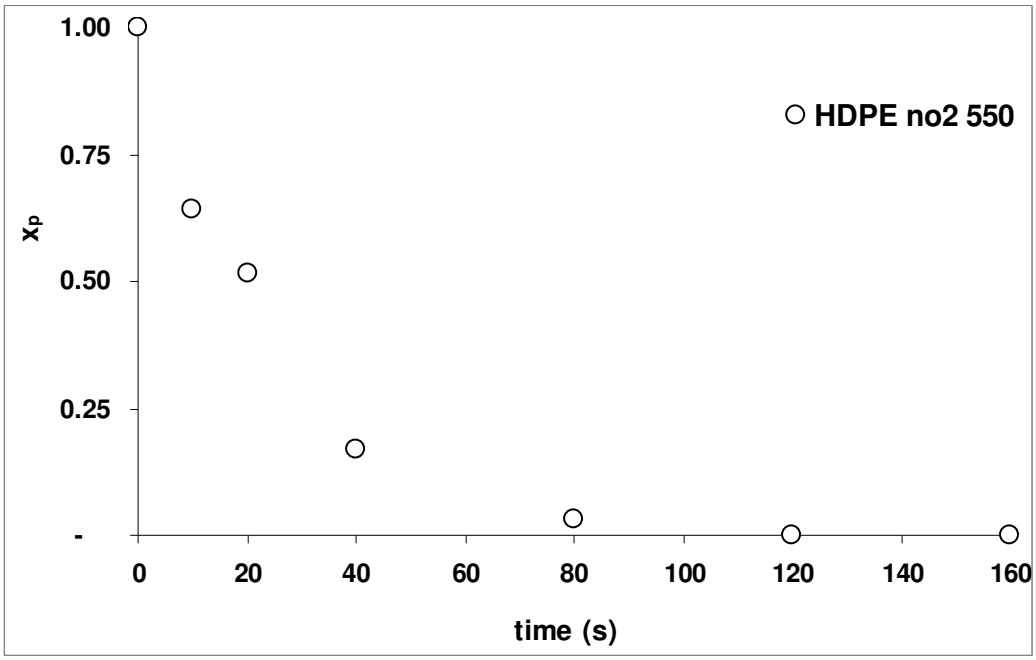

Figure 3.6 - Experimental data (HDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 550°C.

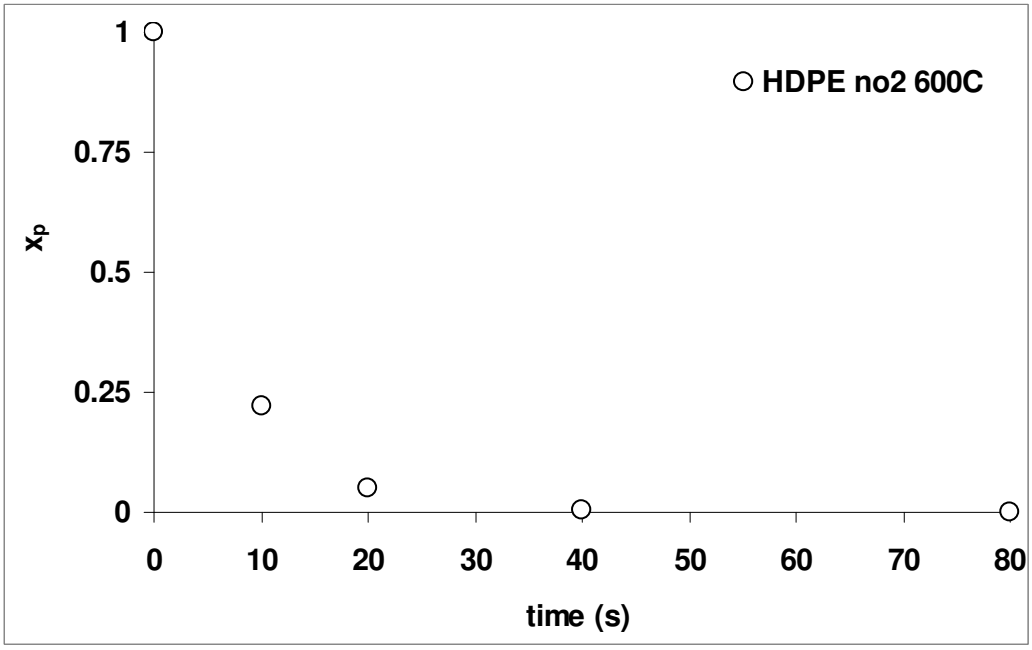

Figure 3.7 - Experimental data (HDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 600°C.

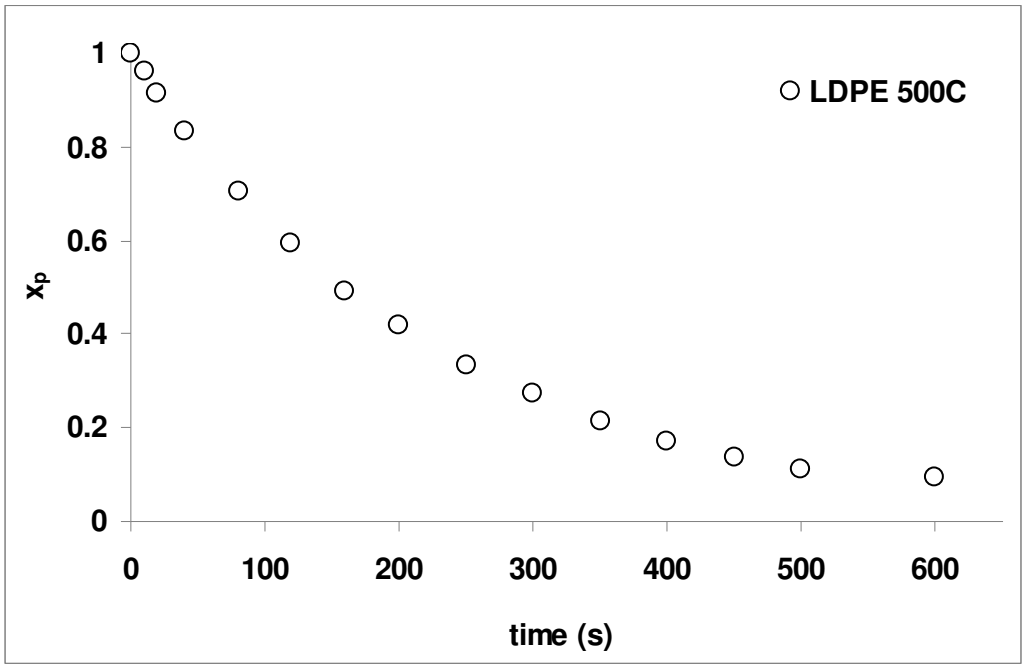

Figure 3.8 - Experimental data (LDPE) showing polymer fraction (x_p) as a function of time (s) at 500°C.

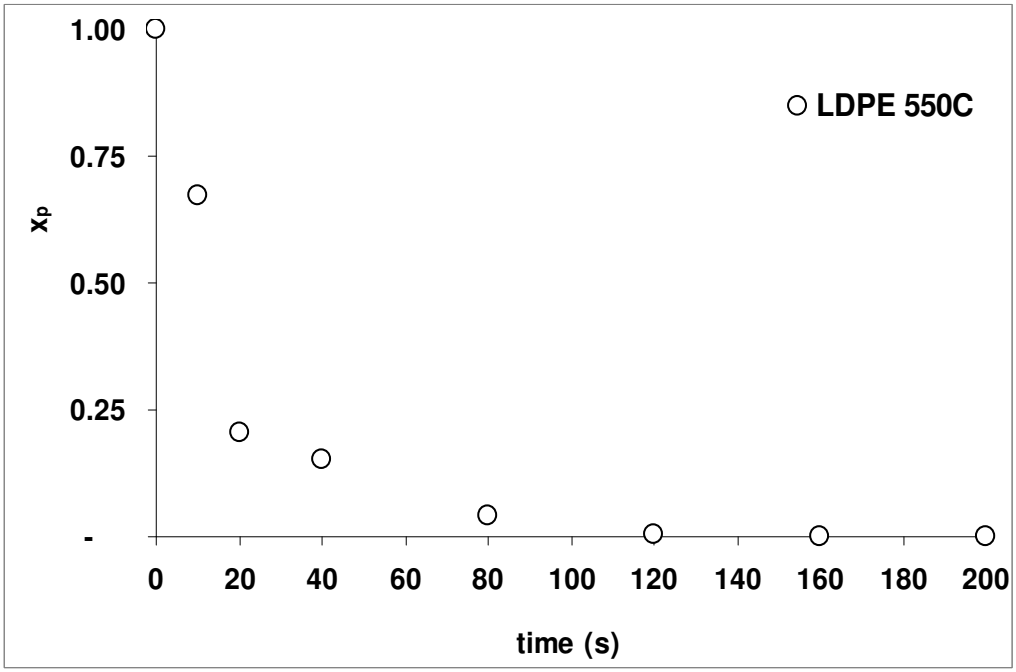

Figure 3.9 - Experimental data (LDPE) showing polymer fraction (x_p) as a function of time (s) at 550°C.

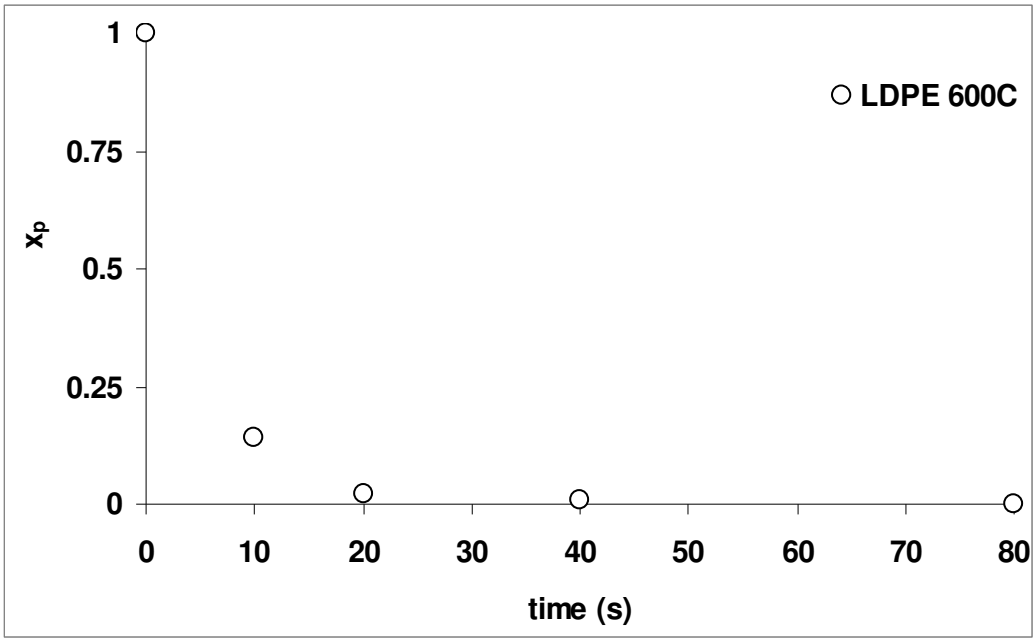

Figure 3.10 - Experimental data (LDPE) showing polymer fraction (x_p) as a function of time (s) at 600°C.

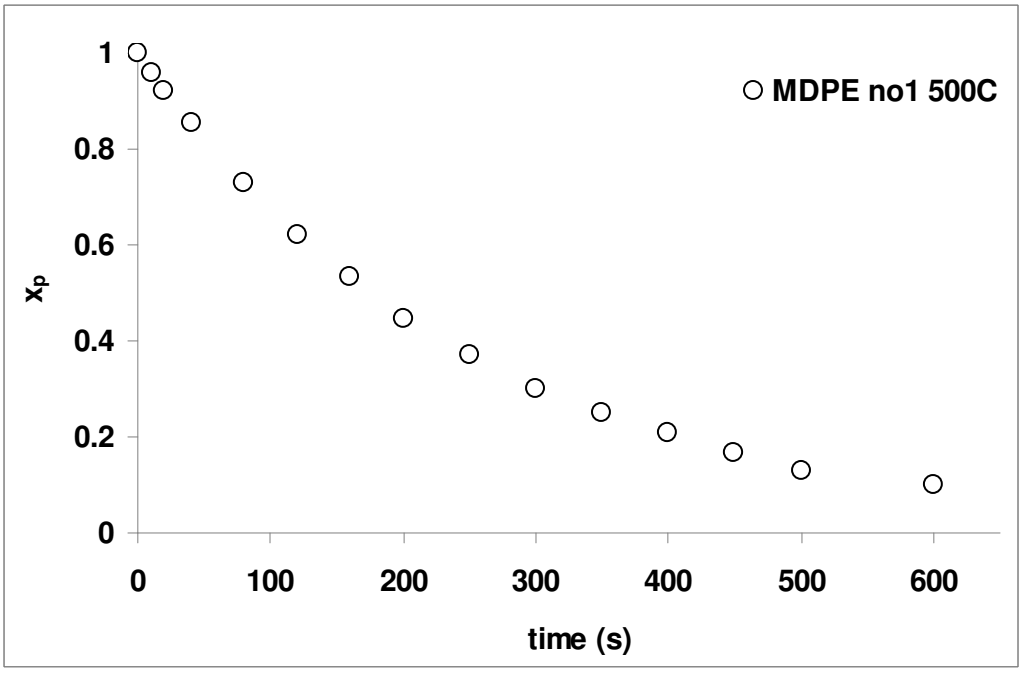

Figure 3.11 - Experimental data (MDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 500°C.

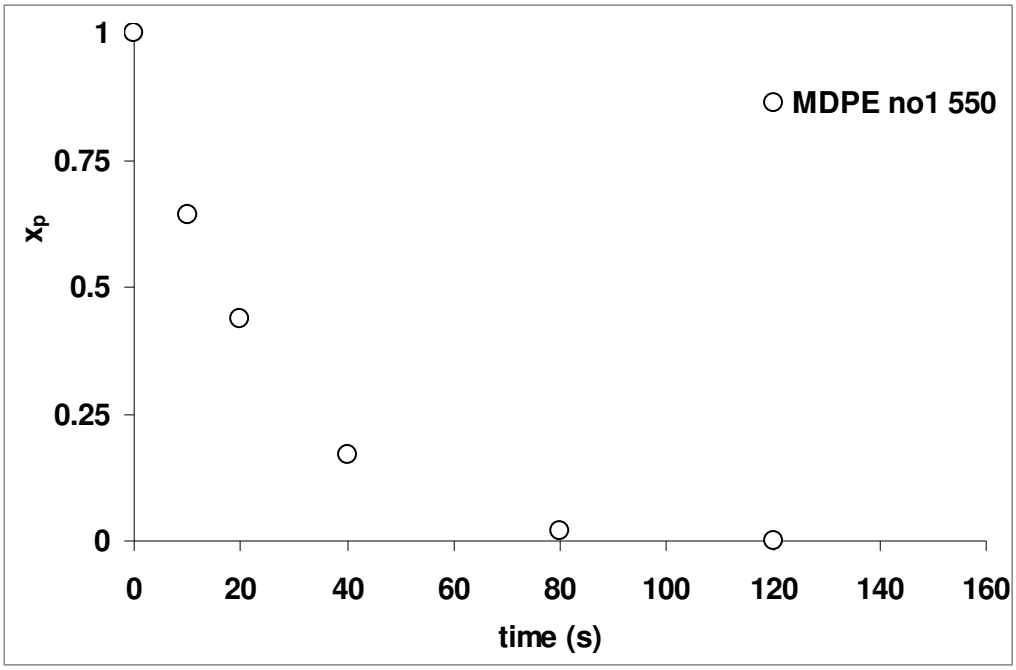

Figure 3.12 - Experimental data (MDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 550°C.

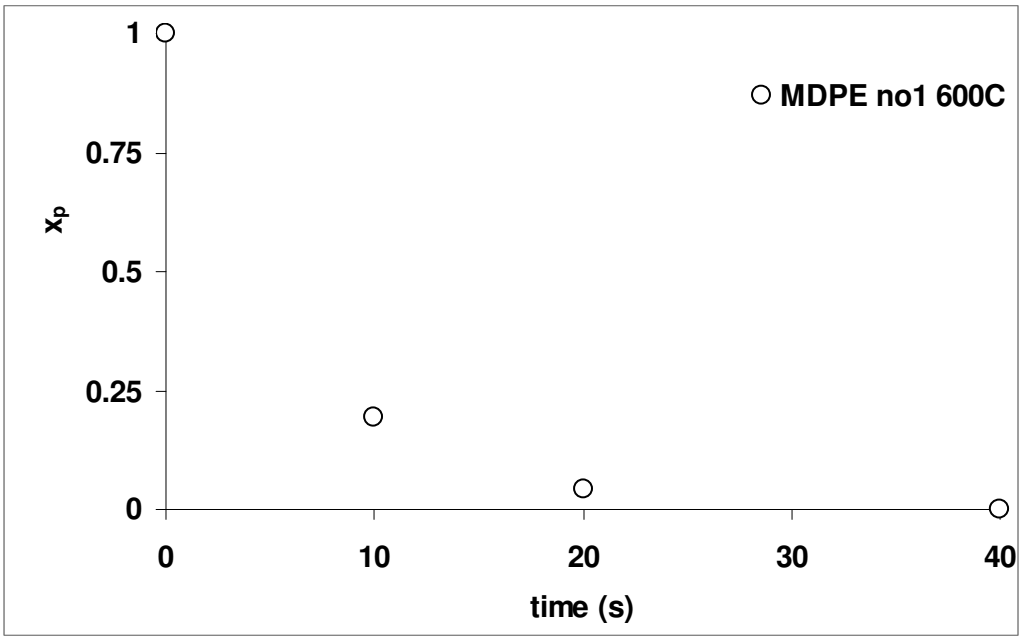

Figure 3.13 - Experimental data (MDPE no.1) showing polymer fraction (x_p) as a function of time (s) at 600°C.

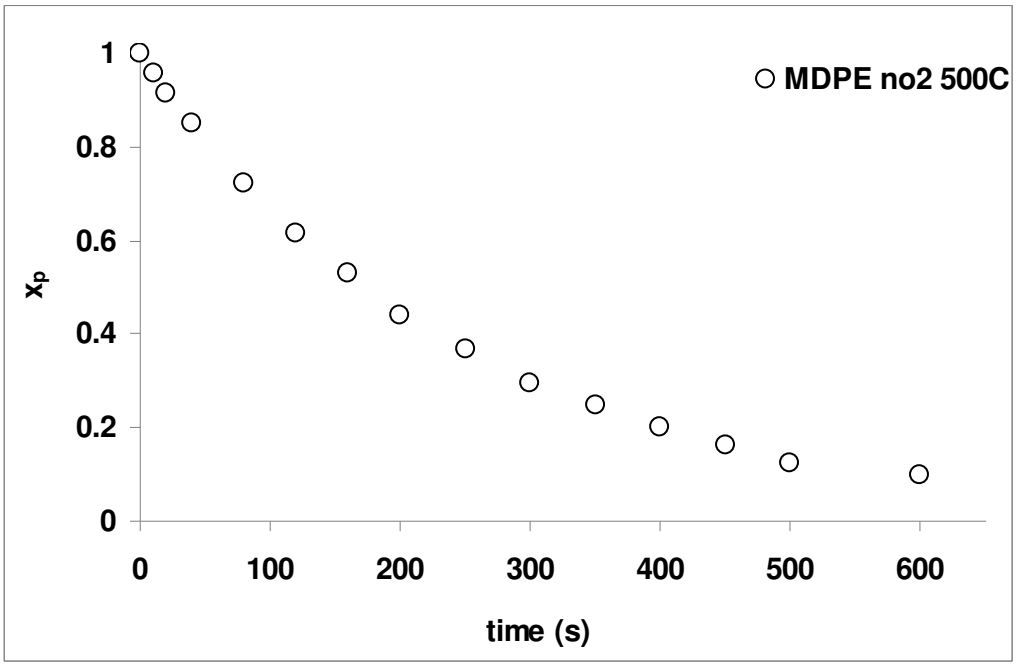

Figure 3.14 - Experimental data (MDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 500°C.

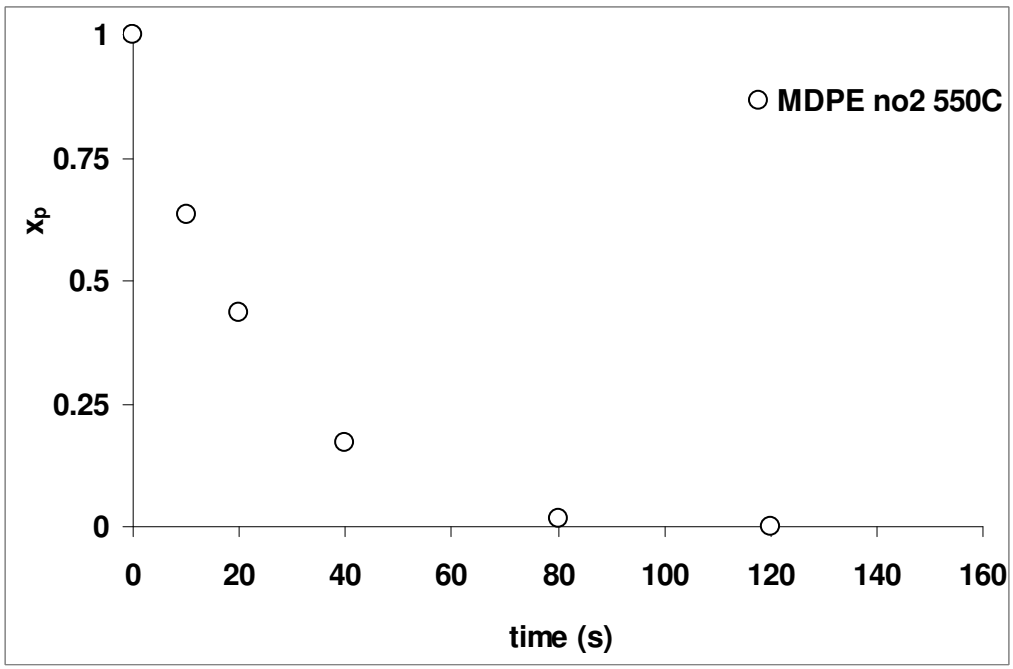

Figure 3.15 - Experimental data (MDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 550°C.

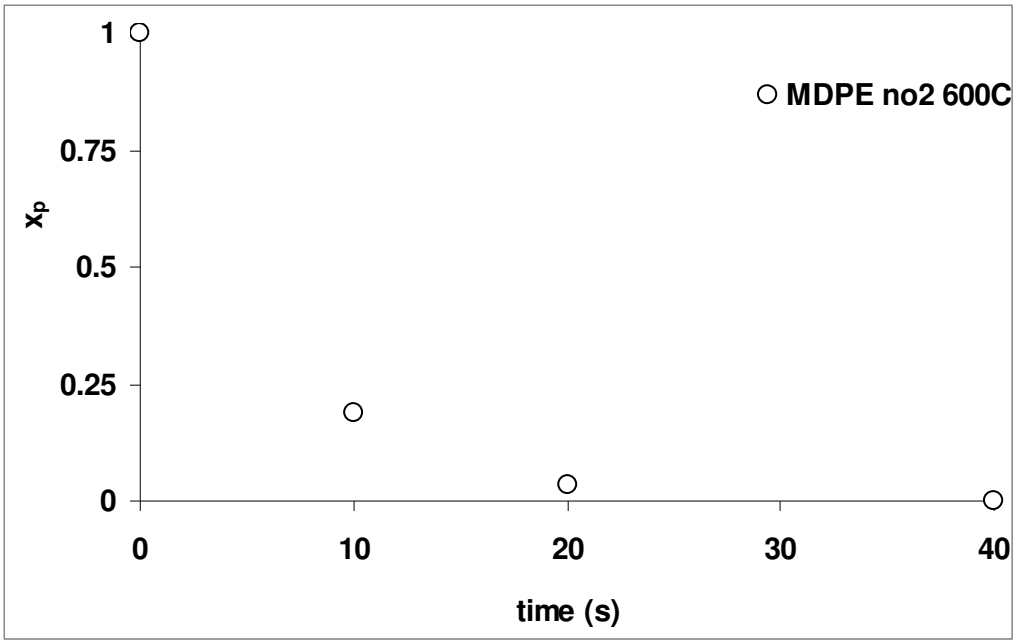

Figure 3.16 - Experimental data (MDPE no.2) showing polymer fraction (x_p) as a function of time (s) at 600°C.

Figure 3.17 shows the products collected experimentally for HDPE no.1, where wax formation was witnessed to decrease with increasing temperatures, although the gas yield increased with increasing temperatures. Figure 3.18 shows the products formed for HDPE no.2. Comparatively, a similar pattern was witnessed between the two HDPE grades in terms of temperature effect on product formation. HDPE no.2 resulted in a higher amount of wax compared to HDPE no.1 being formed at 500°C and there was a similar observation for 550°C and 600°C.

Figure 3.19 shows the pyrolysis product formation for LDPE, and Figures 3.20-3.21 show the product formation resulting from the two RMDPE grades studied. In the case of LDPE, waxes ranged between 68.8 to 50.4 wt% (from 500°C to 600°C), and a similar pattern for the production of waxes was noted for the HDPE grades (Figures 3.17-3.18). The waxes formed as a final product were slightly higher for LDPE (50.4 wt% at 600°C) compared to the other two virgin grades of HDPE (48.7 wt% for HDPE no.1 and 44.1 wt% for HDPE no.2).

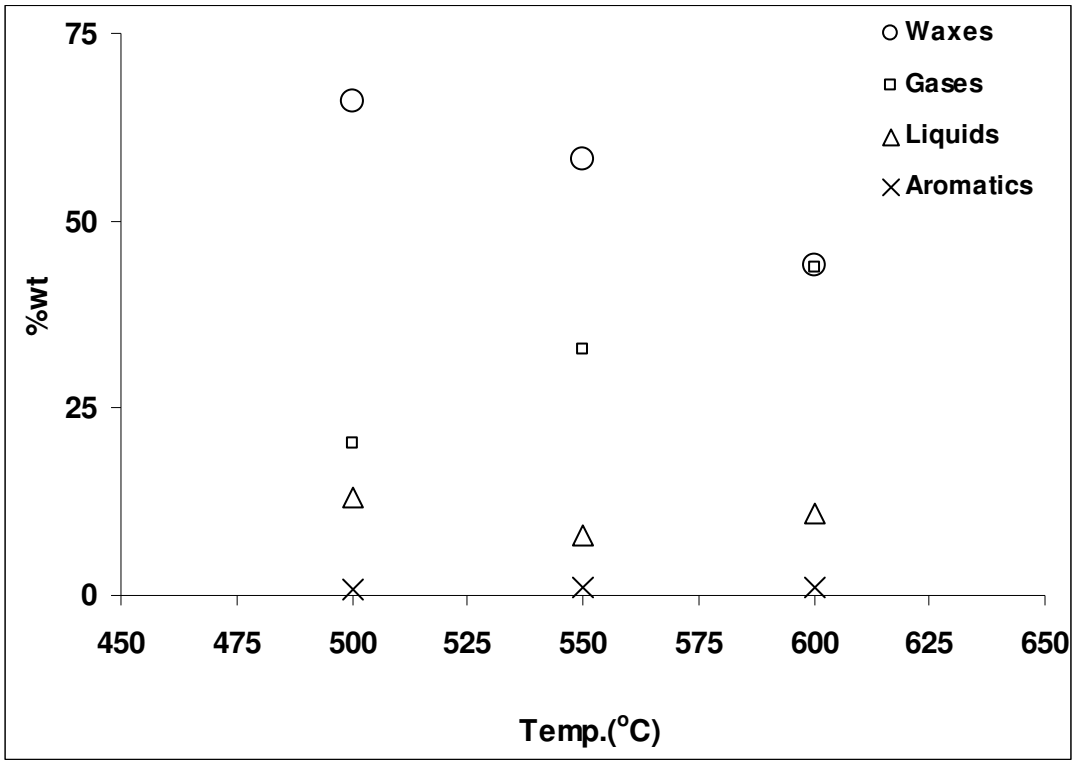

Figure 3.17 – Product fractions collected experimentally for HDPE no.1 as a function of temperature (°C).

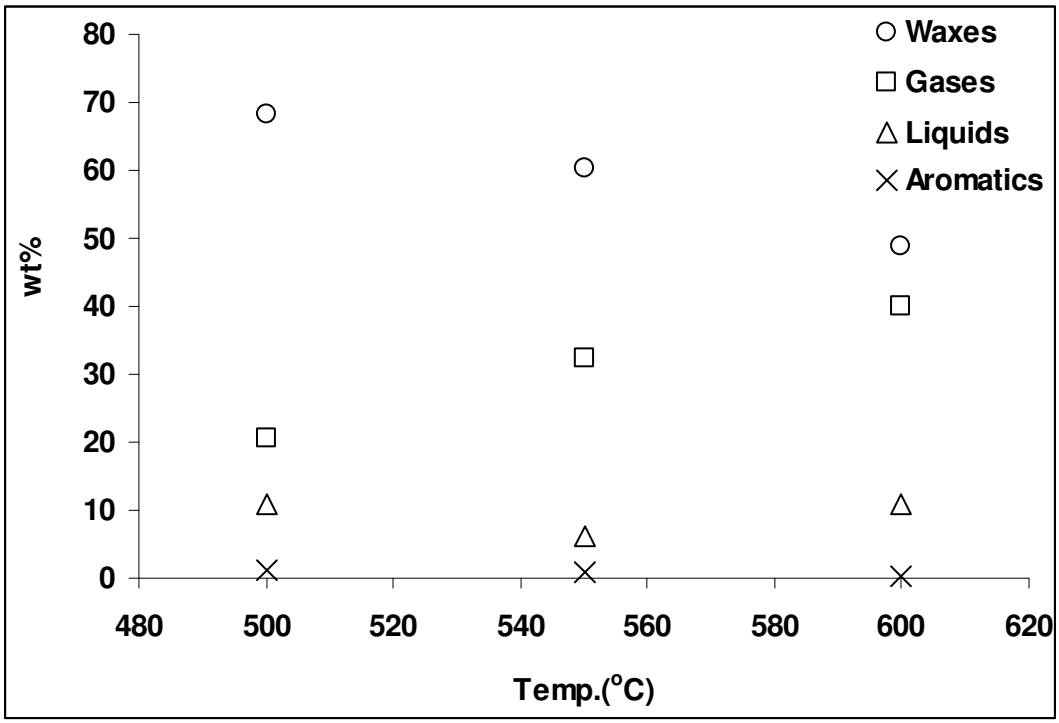

Figure 3.18 - Product fractions collected experimentally for HDPE no.2 as a function of temperature (°C).

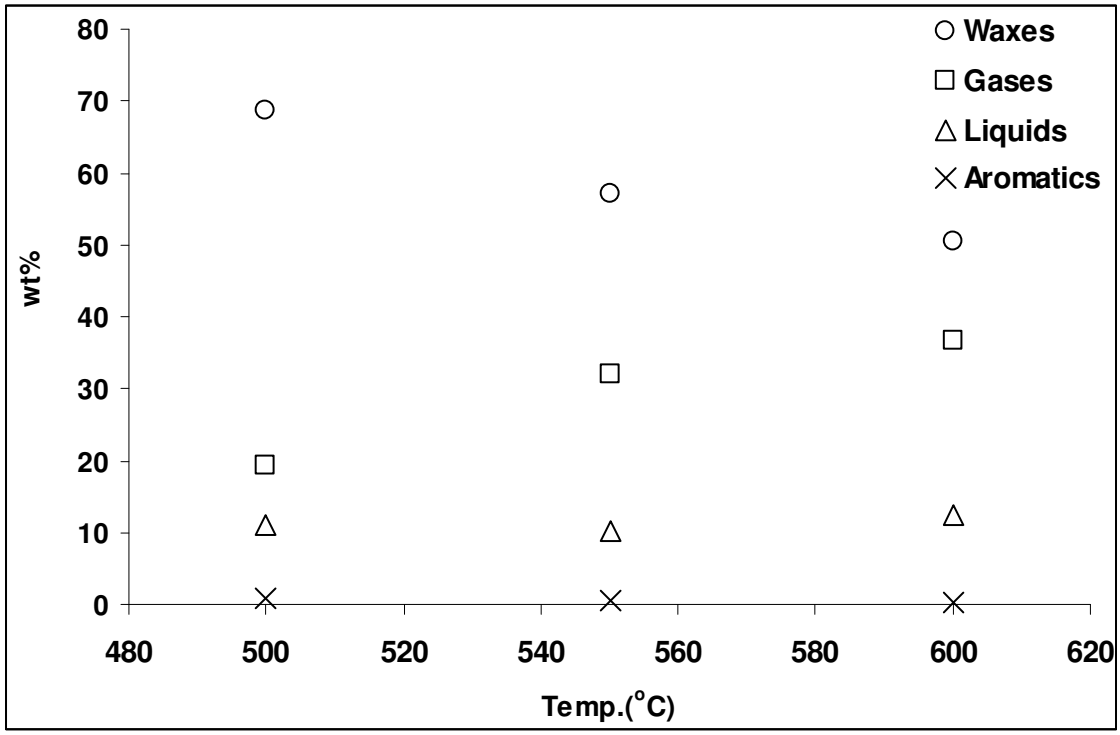

Figure 3.19 - Product fractions collected experimentally for LDPE as a function of temperature (°C).

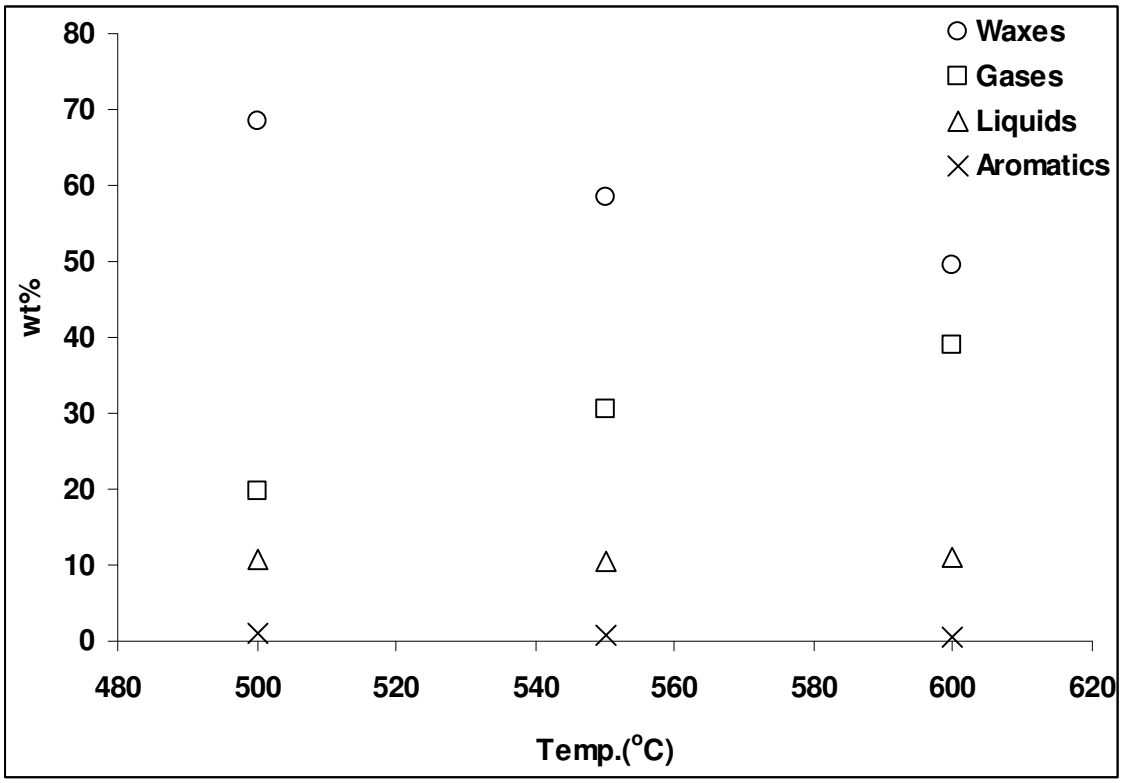

Figure 3.20 - Product fractions collected experimentally for RMDPE no.1 as a function of temperature (°C).

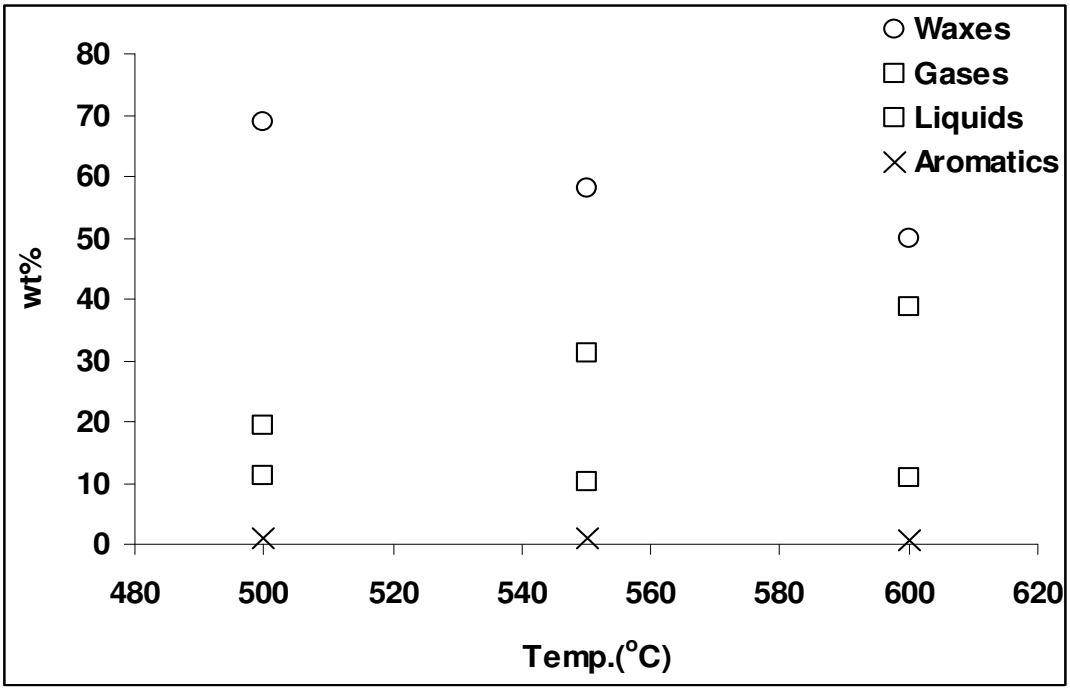

Figure 3.21 - Product fractions collected experimentally for RMDPE no.2 as a function of temperature (°C).

Both RMDPE grades showed a similar pattern in terms of pyrolysis products collected (Figures 3.20-3.21). The difference between the waxes, gases and liquids fractions is negligible when comparing the two RMDPE grades. In comparison, LDPE produced the highest amount of wax at 600°C, i.e. 50.4 wt% and HDPE no.1 produced the highest amount of gases at 600°C (44.1 wt%). Both RMDPE grades did not exceed 39 wt% in the gas fraction. In all the polymers tested, the aromatics fractions did not show a noticeable difference between experimental temperatures.

Both RMDPEs produced lower amounts of liquids and aromatics compared to the other polymers tested (see Figures 3.17-3.21) and this could be attributed to two reasons. First, this is not the first heat cycle these polymers were exposed to, as producing recyclate grades is the result of a number of heating cycles and conversion processes that result in the final product. The second reason is the difference between commercial grades and laboratory prepared pure polymers. The presence of additives in the commercial grades affects the behaviour of the polymers under heating conditions. One of the main reasons for adding additives is to stabilise the polymer and preserve the integrity of the plastic when exposed to a direct heating source.

3.2. A Novel Approach in Isothermal Kinetics: Lumped Product Analysis

Numerous attempts have been undertaken to develop a thermal degradation scheme, usually via a simple approach of parallel reactions from polymer to products (McCaffrey et al., 1995; 1998; Williams and Williams, 1997; 1999a; 1999b; Horvat and Ng, 1999). However, differences are always present due to variations in the characteristics of polymers (e.g. molecular weight, presence of weak links, additives, etc.) and differences in experimental conditions from which kinetic data are calculated (McCaffrey et al., 1995). In this work, a model of the n^{th} order is proposed based on the experiments conducted by Ravago Plastics Co. The model determines the fractions of polymer (x_p), liquids (x_l), gases (x_g), waxes (x_w) and aromatics (x_a) produced. The model is based on the lumped products produced by the pyrolysis experiments.

The product formation analysis was considered from an engineering perspective using lumped product analysis, and kinetics parameters were evaluated accordingly. The mechanism employed in the current study is illustrated in Equation (3.1). It was assumed that the polymer will form the waxes as an intermediate product, which will then progress to produce the other lumped products (gases, liquids and aromatics).

$$(P) \xrightarrow{k_1} (W) \begin{bmatrix} \xrightarrow{k_2} (G) \\ \xrightarrow{k_3} (L) \\ \xrightarrow{k_4} (A) \end{bmatrix} (L) \quad \xrightarrow{k_5} G \tag{3.1}$$

where P, G, L, W and A; stand for the polymer, gases, liquids, waxes and aromatics. k_1, k_2, k_3, k_4, k_5, represent the kinetic rate constant (s^{-1}) of the polymer thermal degradation to waxes (primary reaction) forming an intermediate (molten) stage; waxes to gases, liquids and aromatics (secondary reactions), liquid to gases (tertiary reaction). The subscripts denote the reaction path.

The mathematical model of the mechanism proposed was based on mass balances and rate equation analysis and all reactions were assumed to be irreversible. Derivation of the model was based on mass fractions. The model was developed as a set of ordinary differential equations. The derivation of the model was based on kinetic rate equation mass balance on each component considered, i.e. polymer, waxes, gases, liquids and aromatics. Similar kinetic derivation was undertaken in the past (Bockhorn et al., 1999; Van de Velden et al., 2008). The

model developed is shown in Equations (3.2-3.6). The novelty of this model is to develop a lumped product approach to polymer pyrolysis, in order to understand the product formation mechanism.

$$dx_p/dt = -k_1 x_p^n \quad (3.2)$$

$$dx_w/dt = k_1 x_p^n - (k_2 x_g + k_3 x_l + k_4 x_a) \quad (3.3)$$

$$dx_g/dt = k_2 x_w + k_5 x_l \quad (3.4)$$

$$dx_l/dt = k_3 x_w - k_5 x_l \quad (3.5)$$

$$dx_a/dt = k_4 x_w \quad (3.6)$$

The model was solved using Matlab software (version 7.6 2008) by applying the ODE45 build-in function for a number of non-linear first order differential equations (4^{th} order Runge-Kutta method). To represent the experimental polymer fraction (x_p) throughout the reaction time, theoretical fits were developed. The theoretical fits of polymer fractions (x_p) at each temperature were input in the software, as well as the model equations (non-linear ordinary differential equations, Equations 3.2-3.6). The optimised solution in Matlab for the kinetic rate constants (k_1-k_5) and the reaction order (n) is a function of the rate equations and the reaction order (Equations 3.2-3.6). The absolute error between the theoretical fit and the software solution was minimized as an objective function by Matlab using Fminsearch, ODE-45 method, resulting in the highest regression coefficient (R^2) obtained between the experimental (represented by the theoretical fits) and model solution for the polymer fraction (see results for all materials in Annex A and theoretical fits in Annex B). The software generated the optimized kinetic rate constants (k_1-k_5) and the reaction order (n) for the detailed degradation mechanism studied, as well as the polymer and products fractions as a function of time (s).

In mathematical terms, the optimisation problem is posed in Matlab as follows:

$$\text{Objective Function (O.F.)} = \min \sum_{i=1}^{N} \left| \frac{x_{P(exp)} - x_{p(th)}}{x_{p(exp)}} \right| \tag{3.7}$$

subject to

$$k_i \geq 0 \tag{3.8}$$

$$t_o = 0 \tag{3.9}$$

$$x_{p_1}(t_o) = 1 \tag{3.10}$$

$$x_{g_0}(t_o) = x_1(t_o) = x_a(t_o) = x_w(t_o) = 0 \tag{3.11}$$

$$x_i(t_i) \geq x_{i-1} \tag{3.12}$$

where N is the number of time steps between initial reaction time (t_o) and final reaction time (t_f), $x_{p(exp)}$ is the experimental polymer fraction, $x_{p(th)}$ is the theoretical polymer fraction resulting from the set of differential equations (3.2.-3.6.), k_i are the kinetic rate constant of the differential equations and are determined with the reaction order (n) by the software Matlab using built-in functions (Fminsearch) and (ODE 45), $x_p(t_o)$ is the polymer fraction at time equal to zero (start of reaction), x_i is the product fraction at time equal to or greater to zero. The objective function is set as the sum of error between the experimental and theoretical polymer fractions as depicted in Equation (3.7). Equations (3.8-3.12) represent the optimisation bounds for the kinetic rate constants, initial reaction time, polymer and products fractions, respectively. The product fractions are calculated as a function of the rate equations, resulting in the highest regression coefficients (see Appendix A).

The approach developed in this thesis of lumped product analysis eliminates concerns regarding thermal lag. This is due to the focus being on the final products obtained at a certain operating temperature and the determination of the activation energy of the reaction to validate the mechanism proposed (Equations 3.2-3.6). The main goal of the kinetics modelling detailed in this chapter is to establish a model that is applicable to different grades of PE and which could easily be used by industrial parties concerned with pyrolysis reactor development.

3.3. Results & Discussion

3.3.1. Overall Reaction Order (n) Evaluation and Products Formation Patterns

Equations (3.2-3.6) were used for the evaluation of the reaction order (n) of polymer degradation, which was found to be between 0.97-1 (Table 3.2). The secondary and tertiary reactions are assumed to be of order 1 and this is in agreement with the results obtained by various authors. Ceamanos et al. (2002) evaluated the reaction order (n) as between 0.86-1, whilst Westerhout et al. (1997b) determined n to be equal to 1 in their isothermal pyrolysis analysis of different PE grades. Mucha (1976) evaluated the reaction order (n) of two grades of PE in dynamic conditions, and found it to range between 0-1. This is the reason why the reaction order is typically assumed to be equal to 1 in PE pyrolysis at temperatures above 390°C (Urzendowski and Guenther, 1971; Ceamanos et al., 2002).

The kinetic rate constants (k_i) were evaluated and are shown in Table 3.3. According to Van de Velden et al. (2008), the sum of the primary reactions rate constants equals the overall kinetic rate constant (k_o). Hence in this work, the overall rate constant (k_o) is equal to k_1.

Table 3.2 Isothermal reaction order (n) determined via the proposed model of the mechanism described in Eq.(3.1.).

Polymer	Reaction order (n)
High Density Polyethylene (HDPE no.1)	0.97
High Density Polyethylene (HDPE no.2)	0.97
Low Density Polyethylene (LDPE)	1.0
R. Medium Density Polyethylene (MDPE no.1)	0.98
R. Medium Density Polyethylene (MDPE no.2)	0.98

Table 3.3 Results summary of the depolymerization reactions for the studied polymers in isothermal pyrolysis (500-600 °C), showing kinetic rate constants (s^{-1}).

Polymer	T (°C)	$k_1 \approx k_o$	k_2	k_3	k_4	k_5
HDPE no.1	500	0.66×10^{-2}	0.5×10^{-3}	3×10^{-3}	1×10^{-2}	1.1×10^{-2}
	550	2.43×10^{-2}	0.29×10^{-2}	9.7×10^{-3}	4.9×10^{-3}	1×10^{-4}
	600	0.29	1.6×10^{-2}	2.0×10^{-3}	6.0×10^{-4}	0.89
HDPE no.2	500	0.35×10^{-2}	1.9×10^{-3}	4.0×10^{-4}	4.0×10^{-4}	1×10^{-4}
	550	2.65×10^{-2}	4.0×10^{-4}	1.01×10^{-2}	6.00×10^{-4}	1×10^{-4}
	600	0.14	1.04×10^{-2}	2.8×10^{-3}	1.00×10^{-4}	1×10^{-4}
LDPE	500	0.38×10^{-2}	0.40×10^{-3}	3.00×10^{-4}	2.00×10^{-4}	1×10^{-3}
	550	7.78×10^{-2}	6.7×10^{-2}	3.50×10^{-3}	15.00×10^{-4}	0
	600	0.19	0.63×10^{-2}	1.9×10^{-3}	9.0×10^{-4}	1×10^{-4}
RMDPE no.1	500	0.37×10^{-2}	1.3×10^{-3}	4.00×10^{-4}	5.0×10^{-4}	1×10^{-4}
	550	6.55×10^{-2}	0.15×10^{-2}	1.5×10^{-3}	5.36×10^{-5}	1×10^{-4}
	600	0.21	0.62×10^{-2}	6.20×10^{-3}	1.0×10^{-4}	1×10^{-4}
RMDPE no.2	500	0.36×10^{-2}	0.30×10^{-2}	4.00×10^{-4}	1.00×10^{-4}	1×10^{-4}
	550	0.065	0.15×10^{-2}	0.15×10^{-2}	0.15×10^{-2}	1×10^{-4}
	600	0.20	3.2×10^{-2}	17.7×10^{-3}	0	1.7×10^{-4}

The overall kinetic rate constant (k_o) ranged between 0.37×10^{-2} to 0.29 s^{-1} for the various grades of PE studied. This is in agreement with previous findings by Ceamanos et al. (2002), where k_o (s^{-1}) was found to range between 8.3×10^{-5} to 0.98×10^{-2} and Westerhout et al. (1997a), where k_o (s^{-1}) was found to range between 0.05 to 0.34. With regards to the kinetics of the products formation (Equations 3.2-3.6), one can observe the low value of k_5 (liquids to gases formation in tertiary reaction) in the overall kinetic evaluation by comparison to other rate constants (k_i) (Table 3.3). Although the value of k_5 is relatively very small compared to other rate constants, it represents the tertiary reaction contribution for the final gas product, and thus could not be neglected. The overall kinetic rate constant (k_o) was noticed to have a proportional relationship with the temperature. The overall rate constant (k_o) controls the production of waxes and hence controls the production of the other products too. In addition, k_o also represents the polymer loss kinetic rate constant (as presented in Equation 2.3).

3.3.2. Model Prediction Results

It is paramount to observe the behaviour of each product formed and how it corresponds to the polymer loss. Figures 3.22-3.26 present selected model results showing the product formation patterns. Generally, the polymer degrades whilst the products are formed. The wax formation curve reaches a peak point, after which it starts to decrease producing gases, liquids and aromatics at a higher rate. The model as presented in Equation 3.1, is capable of predicting the polymer fraction (x_p) and the products fractions throughout the time course of the experiment, and the mechanism was chosen for its ability to accurately predict the fractions of polymers and products for all polyolefins tested. However, it is virtually impossible to develop a model that will predict polymer fractions and product yields with 100% accuracy for all experimental data. Consequently, it is important to investigate the model results as a function of temperature and type of polymer. It is also very important to investigate the model's prediction at the end of the reaction time. The next section discusses the main findings in terms of experimental and model results of product yields for the different polymers studied.

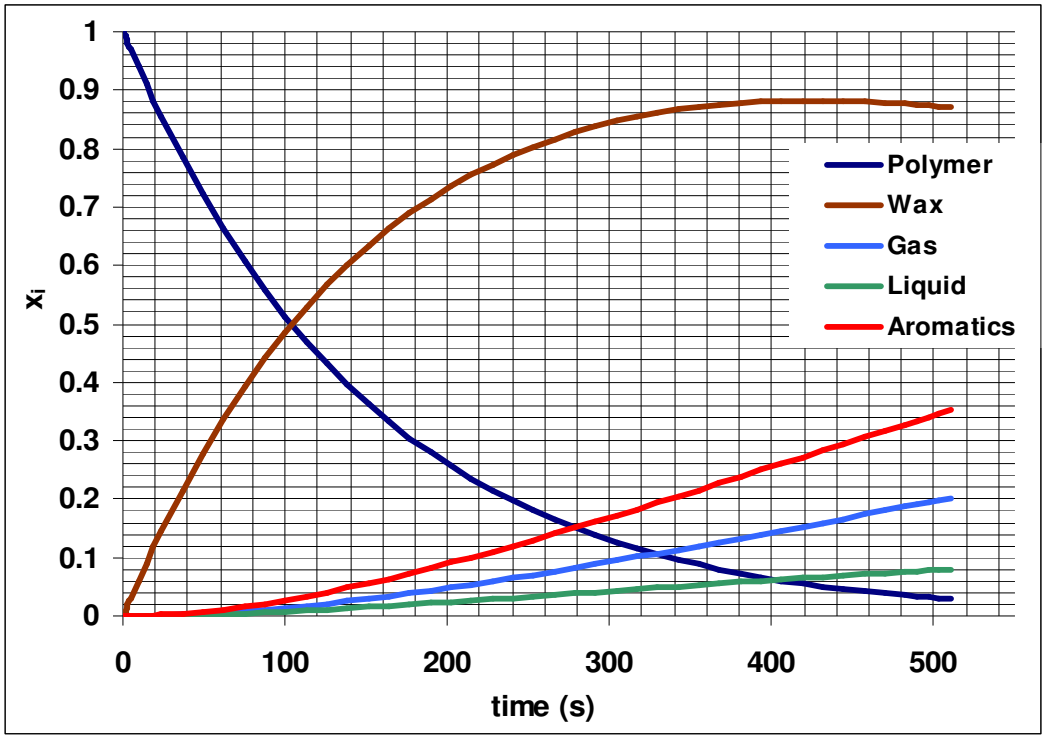

Figure 3.22 - Model result showing product formation and polymer loss as a function of time (s) for **HDPE no.1** at 500°C .

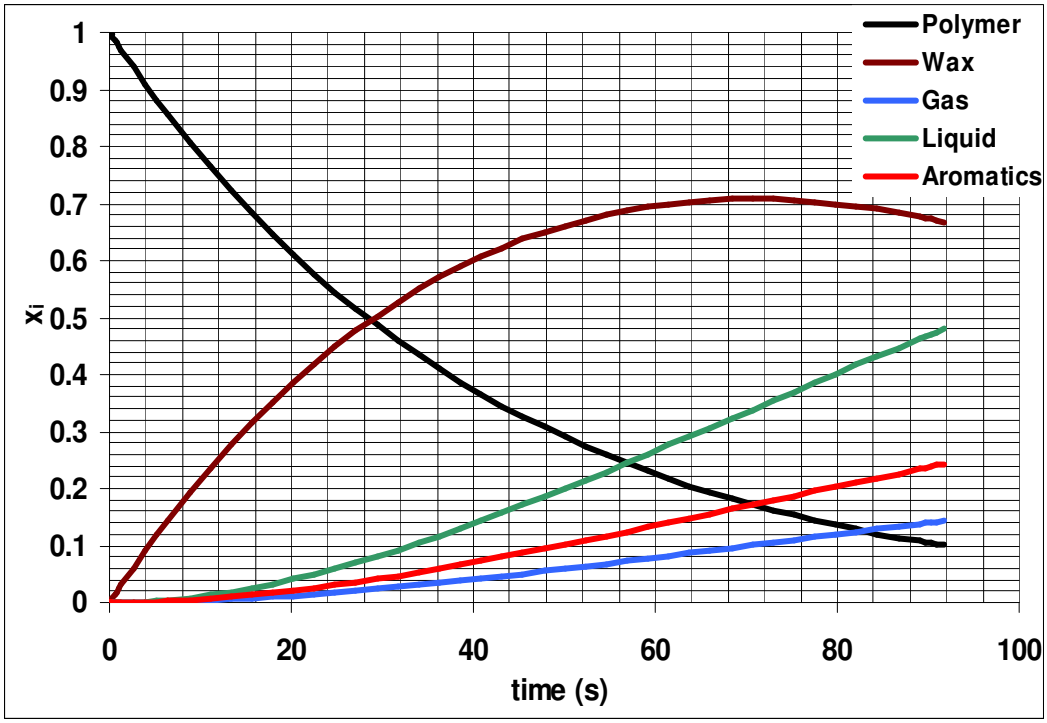

Figure 3.23 - Model result showing product formation and polymer loss as a function of time (s) for **HDPE no.1** at 550°C .

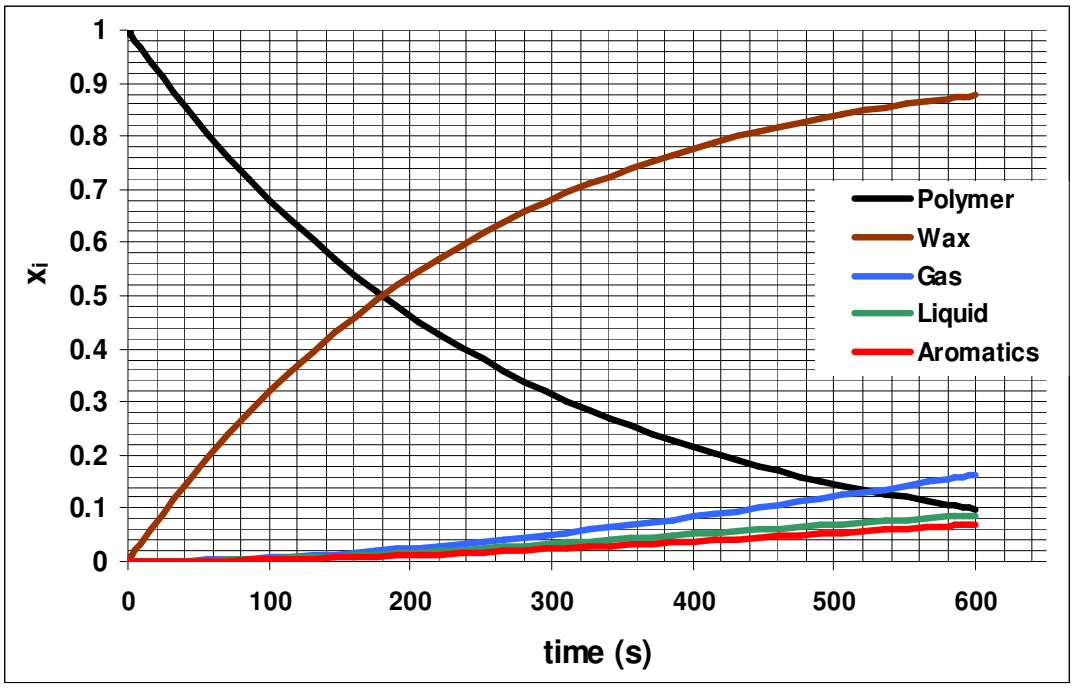

Figure 3.24 - Model result showing product formation and polymer loss as a function of time (s) for **LDPE** at 500°C .

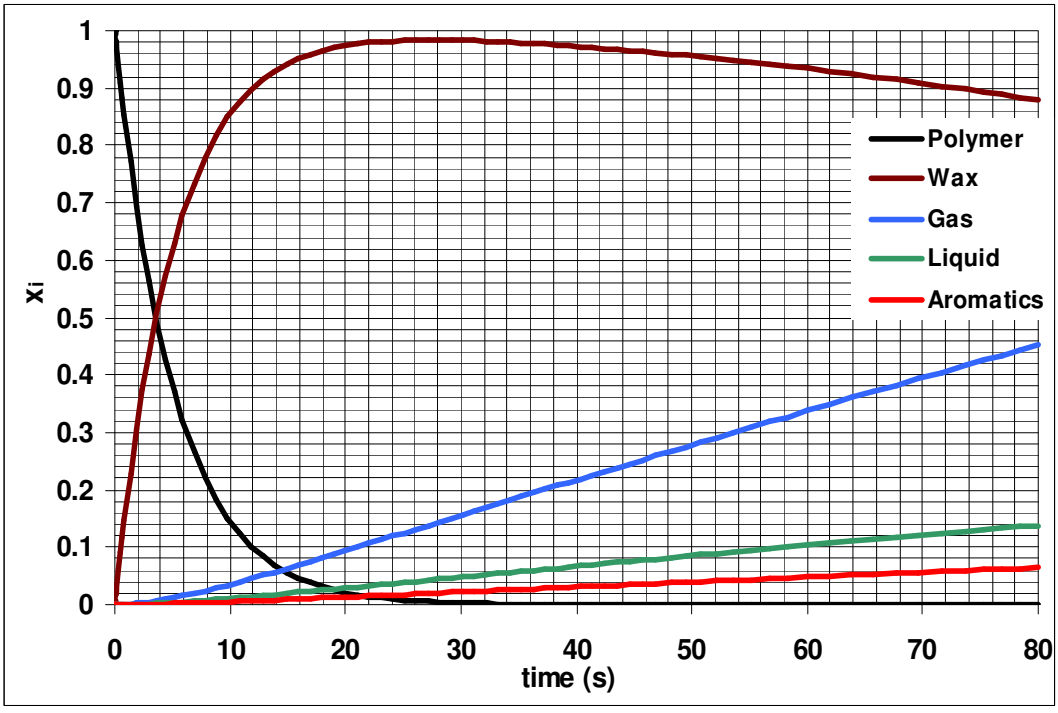

Figure 3.25 - Model result showing product formation and polymer loss as a function of reaction time (s) for **LDPE** at 600°C .

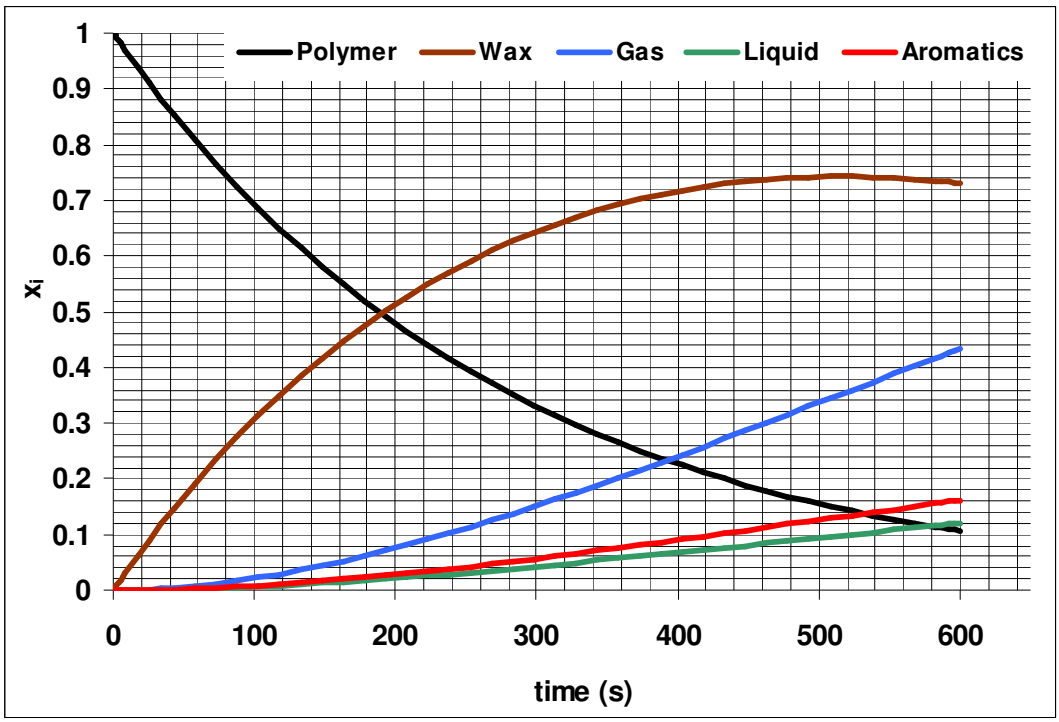

Figure 3.26 - Model result showing product formation and polymer loss as a function of reaction time (s) for **MDPE no.1** at 500°C .

At 500°C, HDPE no.1 reached maximum degradation after 510 s (end of reaction). The final gas fraction (x_g) was found to be 0.20, while the predicted value of the model was determined to be 0.20, resulting in a 0.2% error (Figure 3.22). At the end of the reaction for HDPE no.1 at 550°C, the x_w value was experimentally evaluated as 0.58, whilst the model predicted 0.66, a 13% error (Figure 3.23). At 600°C, the pyrolysis reaction was faster and terminated after 66.3 s. The highest value of x_w was 0.96 at 15.6 s. However, the final x_w was determined as 0.52, with a 18% error from the experimental value of 0.44.

As for HDPE no.2, the wax curve peaked at 389 s with a wax fraction (x_w) value predicted to be 0.65 at 500°C. The gases and liquids fractions increased during the reaction. The waxes fraction (x_w) had a final value of 0.68 (experimental) and 0.58 (model), resulting in a 15% error. The final liquid fraction (x_l) was estimated to be 0.11 by the model, with a 1% error from the experimental value (x_l =0.11). Comparatively, the wax formation in HDPE no.2 peaked some 130 s later than HDPE no.1. The reaction time was also about 100 s higher, which explains the delayed wax formation. The delayed reaction time resulted in a lower value of wax peak too, some 20% less at peak point compared to HDPE no.1. The long reaction times by comparison with HDPE no.1 for 550°C and 600°C, resulted in a longer time for the waxes formed to reach their peak value. At 600°C, the final aromatics fraction (x_a) for HDPE no.1 was determined by the model as 0.004. This results in a 0% error from the experimental value (x_a = 0.004). The

final polymer fraction (x_p) was determined as 0 by the model, resulting in a 0% error from the experimental value.

With regards to the LDPE, the model prediction results at 500°C were as follows: fractions of polymer (x_p), waxes (x_w) and liquids (x_l) were 0.11, 0.58 and 0.12, respectively. The final experimental values for the virgin LDPE at 500°C of the residual polymer, waxes and liquids formed were 0.10, 0.58 and 0.12, respectively, which corresponds to error values of 0.1%, 14% and 8%, respectively. At 600°C, the final predicted value for the aromatics was 0.004, demonstrating a high match with the experimental value of 0.004, and an error of 0%. A 0% error was also calculated between the experimental and model result for the polymer fraction (x_p). A rapid decline was also observed for the polymer degradation, similar to the other virgin grades at this temperature (600°C).

As expected, the model prediction values for both recyclate grades studied were very similar. For MDPE nos.1 and, the model predicted the value of 0.58 as a final wax fraction, whilst the experimental data showed a value of 0.68 (a 10% error at 500°C). A value of 0.11 was predicted at 500°C for the liquid fraction of both MDPE grades, resulting in a 1% error from both experimental values of 0.108. A final polymer fraction was estimated by the model as 0.11 for both MDPE nos.1 and 2, resulting in a 0.1% error. Notably, at 600°C the aromatic fraction (x_a) was estimated as 0.004 by the model, resulting in a 0% error between the experimental and model results. Figures 3.27-3.32 show the model vs. experimental values for the polymer fraction (x_p) for selected polymers at different temperatures. Ideally the plotted values should be on the diagonal to show a match between the experimental and theoretical results.

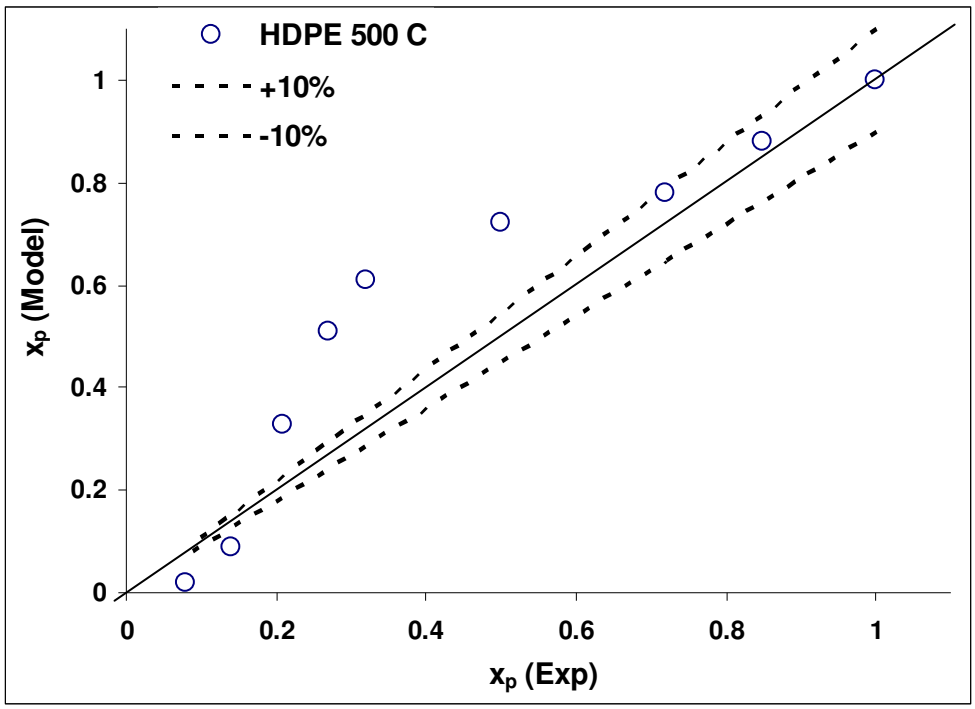

Figure 3.27 - Model vs. experimental values of polymer fraction (x_p) for **HDPE no.1** at 500°C .

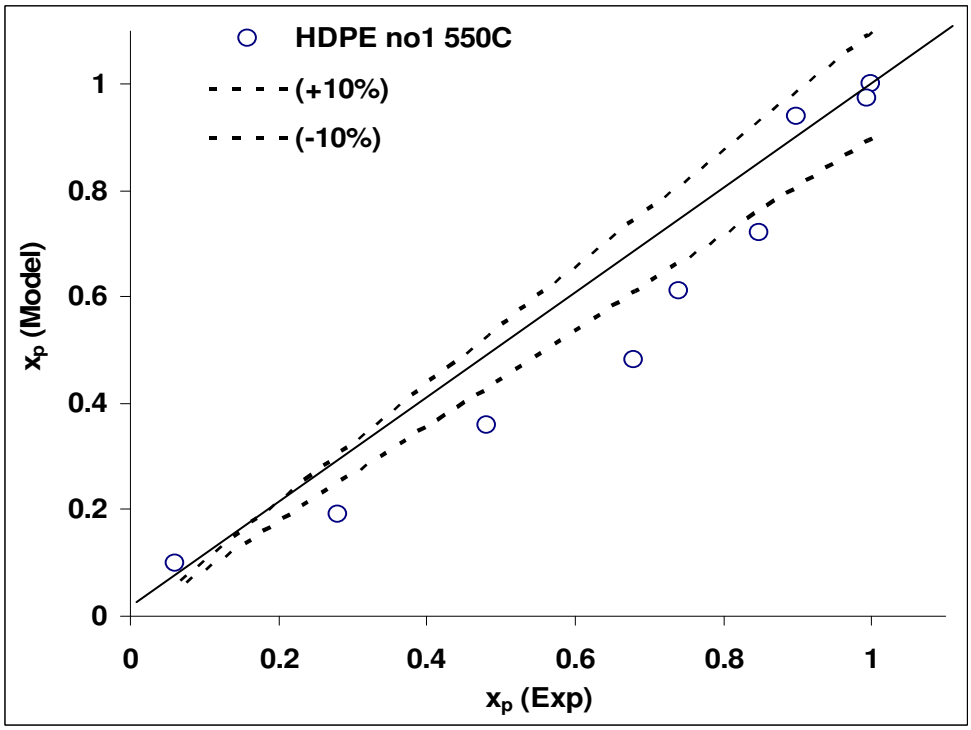

Figure 3.28 - Model vs. experimental values of polymer fraction (x_p) for **HDPE no.1** at 550°C .

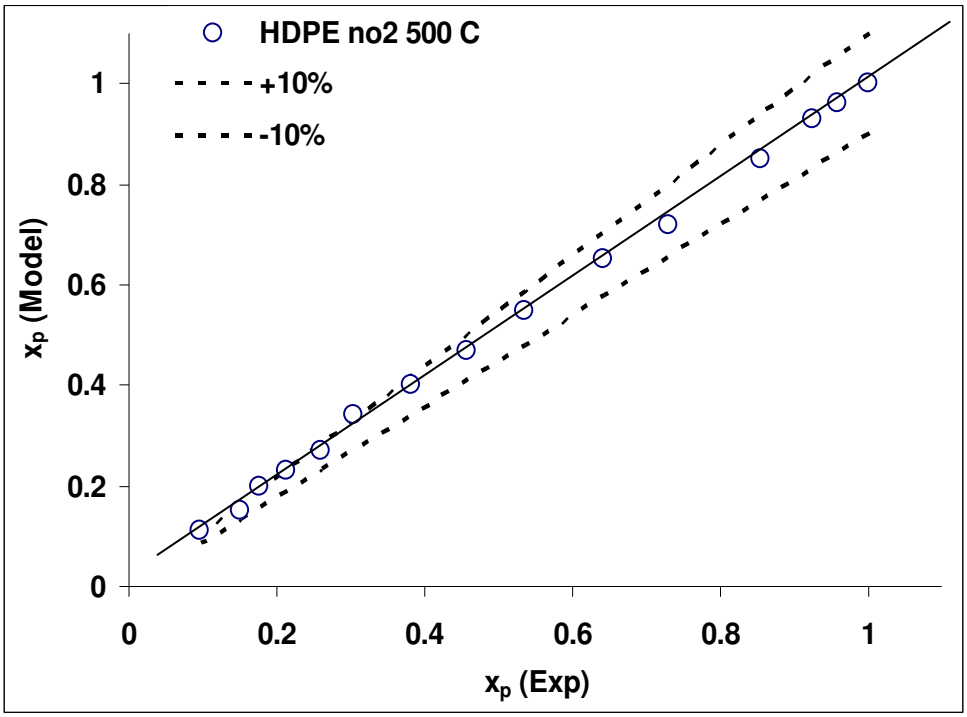

Figure 3.29 - Model vs. experimental values of polymer fraction (x_p) for **HDPE no.2** at 500°C .

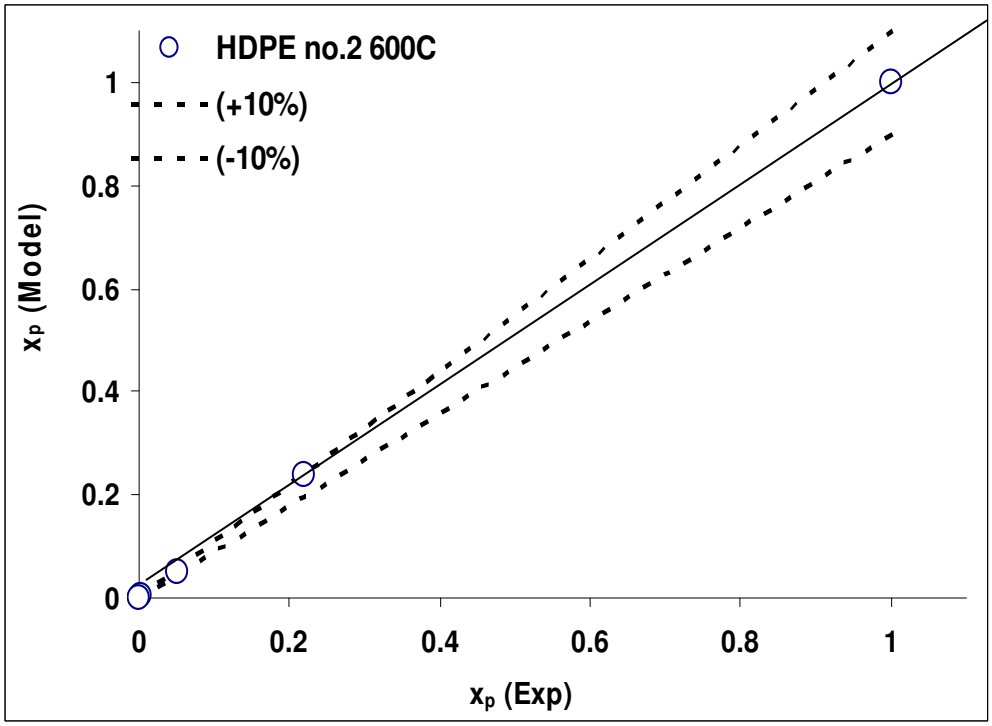

Figure 3.30 - Model vs. experimental values of polymer fraction (x_p) for **HDPE no.2** at 600°C .

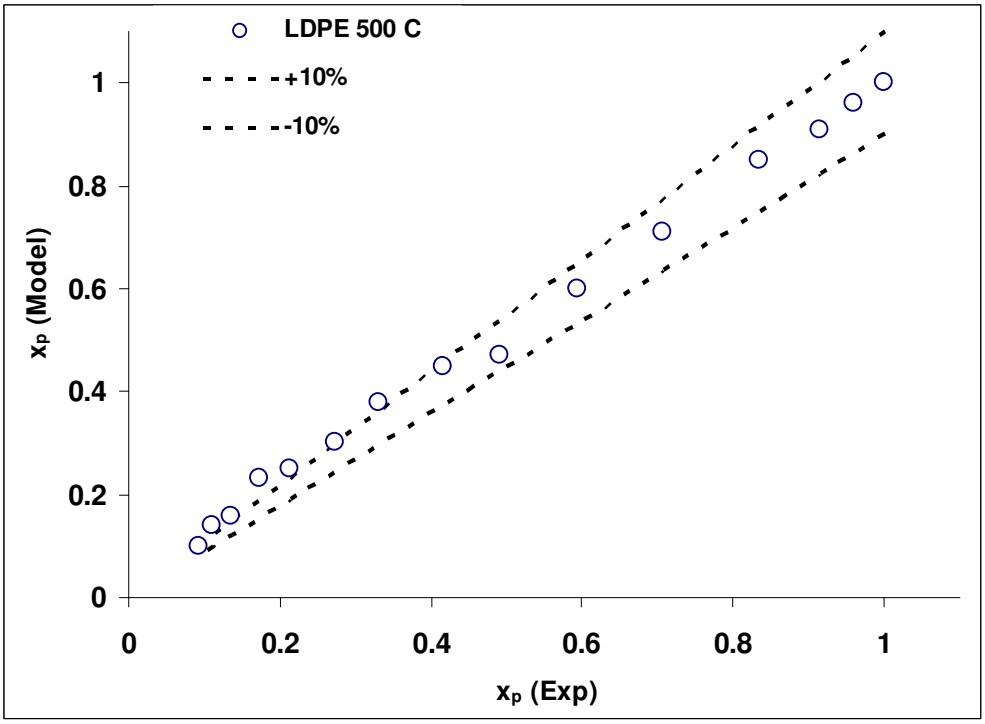

Figure 3.31 - Model vs. experimental values of polymer fraction (x_p) for **LDPE** at 500°C .

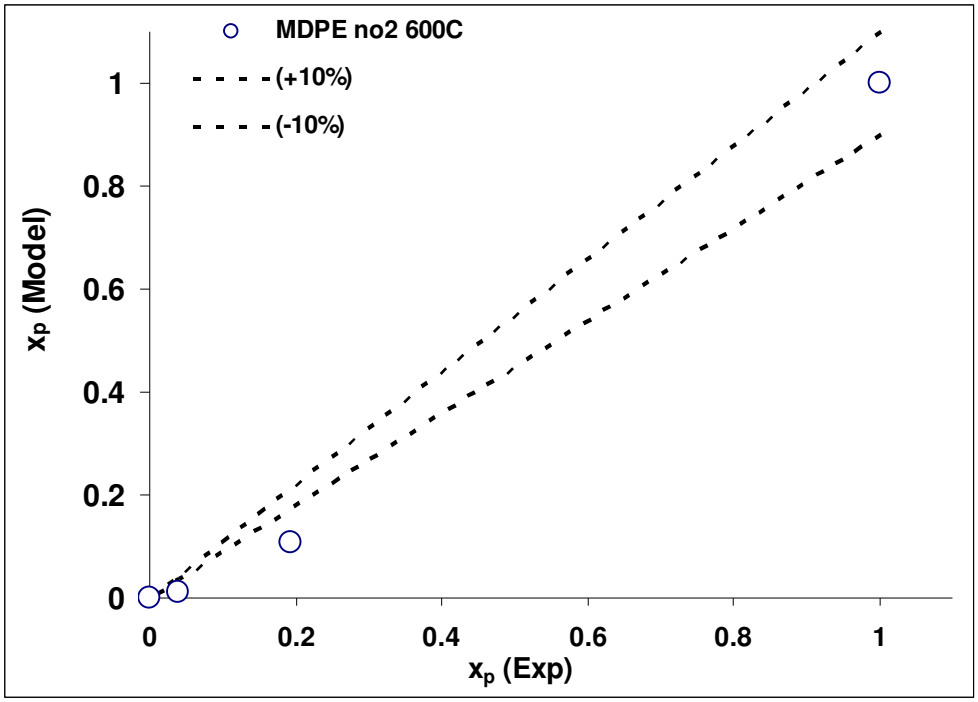

Figure 3.32 - Model vs. experimental values of polymer fraction (x_p) for **MDPE no.2** at 600°C .

HDPE no.1 showed a good match between the experimental and model results for the first 50 s of the reaction at 500°C (Figure 3.27). Observing the behaviour of the two HDPE grades, it was noticed that HDPE no.2 had a smaller margin of error between the experimental and model results at 500°C (Figure 3.29). Results for 550°C and 600°C were all between the ±10% error lines. However, a noticeable deviation occurred at 40 s into the 550°C run. Figure 3.31 shows the results for LDPE, where at 500°C, the results showed almost a perfect match (corresponding with 600 s reaction time) and a ±10% deviation line was appropriate to show the maximum scatter. At 550°C the values plotted were scattered between deviations of ±10% (not shown), although at the start of the reaction, the error values exceed the 10% plotted value. This behaviour is very similar to that of HDPE no.1, MDPE no.1 and no.2 polymers at 550°C, where a ±10% deviation was needed to show the error. Thus, the higher the operating temperatures; the higher the error values and scatter for the model prediction against the experimental values (Figures 3.27-3.32). A very similar model performance was also witnessed for the two recyclate grades (Figures 3.32).

3.3.3. Overall Activation Energy Evaluation

To determine the overall activation energy (E_o) and pre-exponential factor (P_o) for the whole of the reaction, the overall rate constants need to be determined at the operating temperature. The results show that the wax formation rate constant is the overall kinetic rate constant (k_o). Using the Arrhenius first order equation (see Equation 2.3) Figure 3.33 was plotted, which reports the overall reaction kinetics. Table 3.4 summarises the overall reaction kinetics of the polymers studied and Figure 3.34 shows the results with respect to other authors' findings.

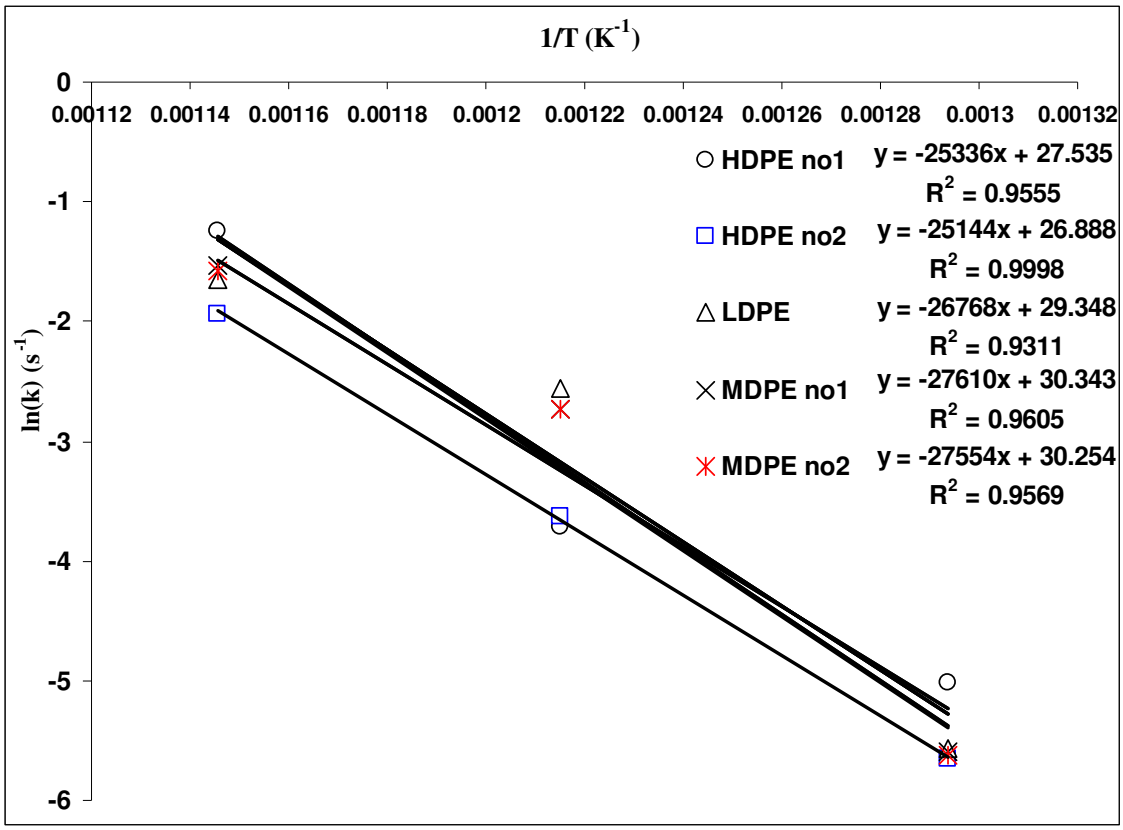

Figure 3.33 - Overall Arrhenius plot (using overall kinetic rate constant, k_o) for polymers tested showing points fitted for overall activation energy (E_o) and pre-exponential factor (P_o) evaluation.

Table 3.4 Overall reaction (rxn) kinetics showing rxn order (n), overall activation energy (E_o) and overall pre-exponential factor (k_o).

Polymer	reaction order (n)	E_o (kJ mol^{-1})	P_o (s^{-1})
HDPE no 1	0.97	211	9.1 x 10^{11}
HDPE no 2	0.97	209	4.8 x 10^{11}
LDPE	1	223	5.6 x 10^{12}
MDPE no 1	0.98	230	1.5 x 10^{13}
MDPE no 2	0.98	229	1.4 x 10^{13}

The results obtained in this study were compared to those of previous researchers, which were obtained using different mechanisms and under different operating conditions. In this work, the overall activation energy ranged between 211 – 230 kJ mol^{-1}, which fell between the range of values found within the literature: Knümann and Bockhorn (1994), 268±3 kJ mol^{-1} for pure PE in isothermal conditions and 262.1±1.9 kJ mol^{-1} for pure PE in dynamic conditions; Westerhout et al. (1997b), 220-241 kJ mol^{-1} for PE in isothermal conditions; Mucha (1976), 247-330 kJ mol^{-1} for HDPE in dynamic conditions and 163-230 kJ mol^{-1} for LDPE in dynamic conditions; and Ceamanos et al. (2002), 248.7 kJ mol^{-1} for HDPE in isothermal conditions, as well as other references reported in Figure 3.34. This shows that the mechanism considered in this work is applicable for different grades of PE.

As previously observed by Ceamanos et al. (2002), Figure 3.34 shows a linear relationship between log (k_o) and E_o which is known as the kinetic compensation effect, and has been considered to be the result of mathematical, physicochemical and experimental causes. The coupling of the kinetic parameters can result in similar values of the kinetic constant, thus the activation energy and pre-exponential (frequency) factor must be considered apparent.

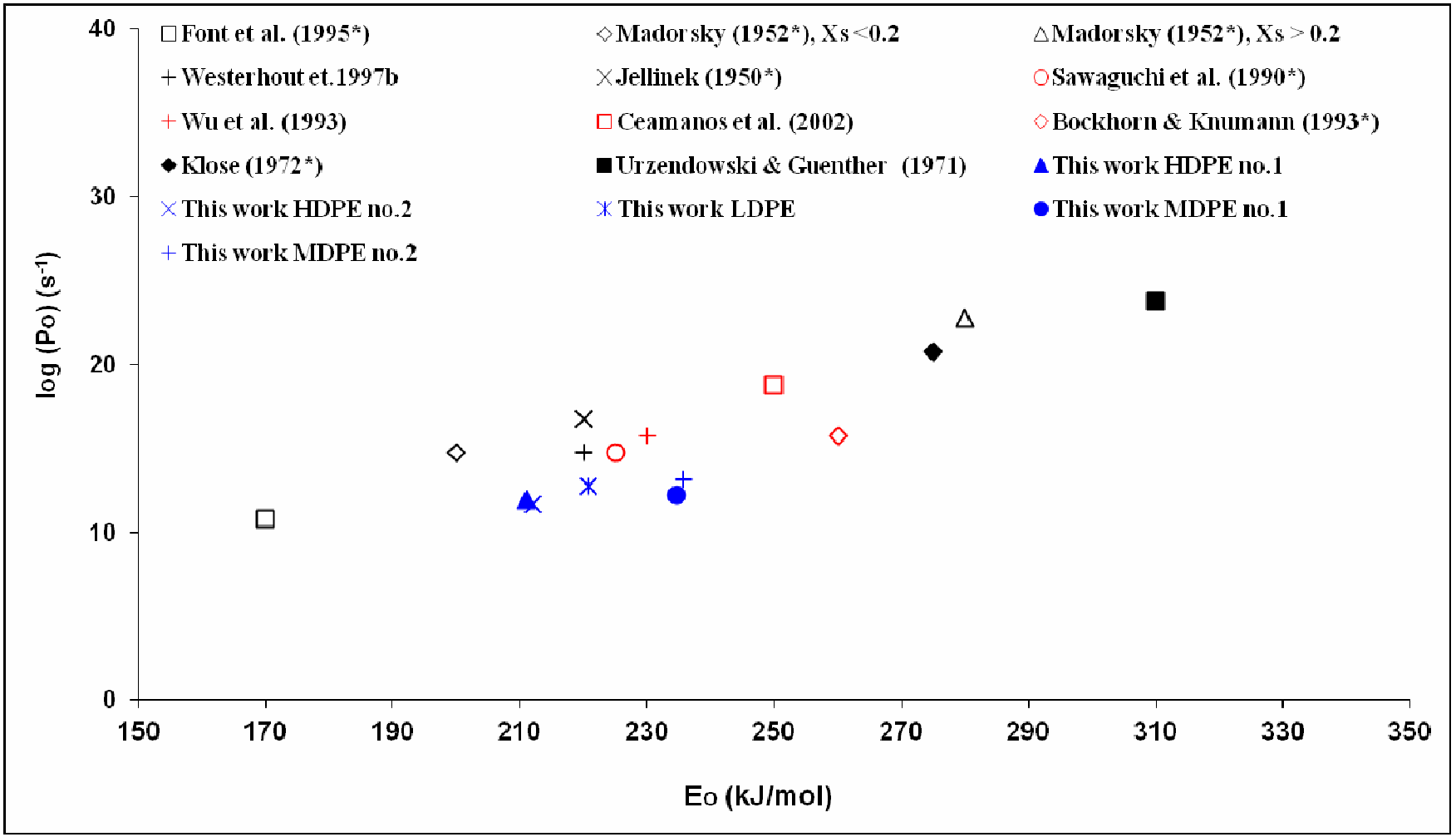

Figure 3.34 - Log (P_o) (s^{-1}) vs. E_o (kJ/mol) obtained by different authors with comparison to this work.
* Taken from Ceamanos et al. (2002).
Notes: - P_o unit in this figure was changed to s^{-1} to be consistent with work reported in this thesis.
- x_s refers to solid conversion in the above stated reference.

3.4. Conclusions

Pyrolysis is considered one of the advanced thermolysis processes in unit operations. It presents a number of advantages, namely the production and obtention of valuable chemicals and is also the focus of the analysis conducted in this thesis. Five polymers were used in this study, namely two virgin grades of HDPE, one virgin grade of LDPE and two recycled grades of MDPE. TGA results at high heating rates and pre-set temperatures (similar to conditions encountered in industrial fast pyrolysis units), was used to:

i. Investigate the thermal cracking behaviour of the polymers studied

ii. Determine the isothermal reaction kinetics associated with the polymers studied

iii. Develop and validate a novel model based on the production and interaction of grouped products yielded by pyrolysis.

The mathematical model of the mechanism proposed was based on mass balances and rate equation analysis, as presented in Equation 3.1. The reaction order (n) of polymer degradation ranged between 0.97-1, and the overall kinetic rate constant (k_o) ranged between 0.37×10^{-2} to 0.29 s^{-1} for the various grades of PE studied. This is in agreement with previous reports by various authors (Westerhout et al., 1997a; Ceamanos et al., 2002; Dahiya et al., 2008). The overall activation energy ranged between 211 – 230 kJ mol^{-1}, which fell within the range of previous findings for PE pyrolysis. In addition, the mechanism proposed also enabled the assessment of the single path reactions of the products formed.

Similar patterns were observed between the two HDPE grades in terms of wax formation, although HDPE no.2 resulted in a higher amount of wax being produced. In the case of LDPE, wax formation ranged between 68.8 to 50.4 wt% (between 500 to 600°C). This is due to the fact that virgin grade LDPE has a lower melting point than virgin grade HDPE, and it melts and forms the intermediate stage (i.e. waxes) quicker than the HDPE grades studied. This was reflected in the wax formation observed in this study. This fact also supports the mechanism proposed, whereby waxes are considered as an intermediate state. The fact that the lower the melting point the higher the amount of wax collected, justifies the assumption of considering waxes as an intermediate.

Chapter 4

On the Isothermal Pyrolysis of End of Life Tyres

Ever since Charles Goodyear announced the discovery of the vulcanisation process back in 1843, tyre production has never stopped growing, which has led to the accumulation of scrap resulting from end of life tyres (ELTs). ELTs embody a high calorific value which makes them ideal for TCT (since over 60% of their structure is polymer based) and energy recovery (via a number of thermal processes). This chapter presents the application of isothermal pyrolysis on ELTs and results obtained via isothermal thermogravimetry are shown. The main objective of this Chapter is to demonstrate the possibility of utilizing a pre-set temperature (T = 500°C) for the pyrolysis process to the benefit of intensifying the global product yields recovered. A degradation mechanism is proposed based on lumped products formed (similar to Chapter 3). Thermal degradation of ELTs was taken from a depolymerisation approach (ELTs encompass a large percentage of polyisoprene polymer). The products of ELTs pyrolysis were lumped into four categories, namely gases, liquids, char and aromatics.

Parts of this chapter were previously published:

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**). Kinetics and product distribution of end of life tyres (ELTs) pyrolysis: A novel approach in *polyisoprene* and *SBR* thermal cracking, *Journal of Hazardous Materials*, **172(2-3)**; 1690-1694.

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**). The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, *Progress in Energy & Combustion Science*, **36(1)**; 103-129.

4.1. Introductory Remark

ELTs contain a high fraction of polymers, namely polyisoprene (PI), polybutadiene (PBD) and a significant proportion of styrene-butadiene-rubber (SBR), with both natural and synthetic rubbers typically present in any commercial grade tyre. The synthetic rubber, which acts as an elastomer to withstand higher deformation, is typically a polymerised material of a variety of monomers (e.g. isoprene (2-methyl-1,3-butadiene), 1,3-butadiene, chloroprene (2-chloro-1,3-butadiene), and isobutylene (methylpropene). SBR is a synthetic rubber made by the co-polymerisation of styrene and butadiene. It has good abrasion resistance and good aging stability when protected by additives, and is widely used in car tyres, where it is blended with natural rubber. SBR can be produced from a solution or an emulsion, but in both instances the reaction is via free radical polymerisation.

Natural rubber derived from latex is mostly polymerised isoprene with a small percentage of impurities in it which limit the range of available properties. In addition, there are limitations on the proportions of *cis* and *trans*[1] double bonds resulting from the methods utilised to polymerise natural latex. This also limits the range of properties available to natural rubber, although these are improved by the addition of sulphur and vulcanisation (i.e. in the case of tyre production). ELTs make up a significant proportion of hazardous solid waste and the question of dealing with this has become ever more prominent. According to the European Tyres and Rubber Manufacturers Association (ETRMA), 3.28×10^6 tonnes of ELTs were produced in the EU and similar estimates were given for the US in 2007. Worldwide, over 65% of ELTs are landfilled or discarded in the open resulting in numerous environmental burdens on their surroundings (Roy et al., 1999; Galvagno et al., 2002). ELTs pose a serious threat to developed societies for their disposal or re-use, because of their shape, size and physicochemical nature, coupled with the fact that they are very hard to recycle in conventional ways (Conesa et al., 2000).

Out of the total volume of ELTs arising in Europe, 34% were used in material recovery facilities in 2007. European Commission (EC) legislative decisions with regards to recycling, landfilling and waste thermal treatments, all address the issue of ELTs. Recent strategies regarding recycling and recovery in Europe (EC 2000-53) all stress better design is required to further develop approaches for the determination of best environmental options and for the setting of ELTs recycling and recovery rates within the EU. They also strongly recommend the implementation of LCA techniques to better utilise certain stages of the life cycle of ELTs to the benefit of both material recovering industries and ELT producers. In 2006, an EU ban on whole

[1] Functional group orientation.

and shredded tyre landfilling came into effect. ELTs are classified as durable products or special waste, and are collected separately from other types of solid waste by private companies that deal with their pre-preparation for thermal treatments. ELTs are often washed to remove debris, glass, stones and burned fragments. Under the EC's waste directives (EC 2008-98; EC 2000-76), the feed to pyrolysis reactors and other thermal units must undergo size reduction processes by concerned parties, and these processes include a two phase treatment. The first is concerned with the car or truck tyres granulation to form chip like feedstock ranging in diameter between 0.1-0.5 mm (for granules). The second is concerned with the process conditions, whereby the unit is set to an optimum outlet zone temperature (for pyrolysis reactors) of between 450-500°C. This ensures that the pyrolytic char produced will be within the specification detailed by the EU market. Despite the well-known molecular chemical composition of natural/synthetic rubber, ELTs embody various "contaminants": for natural rubber these include: S-vulcanisation, vulcanisation accelerators, such as derived from benzothiazole and sulfenamides; ZnO and certain fatty acids; reinforcing agents such as carbon black; and anti-degradants (amines, phenols, or phosphates). Synthetic rubber manufacturing applies either a Ziegler-Natta catalyst ($TiCl_3$ or $TiCl_4$ in combination with an organometallic compound, Et_3Al), peroxide initiators for radical polymerisation or acids for cationic polymerisation. Other metals can also be present, such as sodium (BuNa-S), copper, manganese and nickel. The heating value of rubber is however higher than that of coal and biomass (Berrueco et al., 2005), which makes it an ideal feedstock for pyrolysis, gasification and combustion.

The pyrolysis of ELTs (depolymerisation under an inert atmosphere) is receiving renewed attention for the simple fact that it yields condensable fractions and solid carbon residues highly desirable and easy to market. The solid residue produced may be directly used as a smokeless fuel (Berrueco et al., 2005), carbon black or activated carbon (Cunliffe and Williams, 1998). Although pyrolysis char is desirable in its own market, the presence of heavy metals (as a potential hazard) is usually reduced by further evaporation (Cunliffe and Williams, 1999). Liquid products resulting from ELTs pyrolysis consist of a complex mixture of organic compounds (5-20 carbons) which are very rich in aromatics (single ring structure). Thus, the derived oils can be used as fuels or petroleum refinery feedstock (Cunliffe and Williams, 1999). Further treatment (with rapid quenching) of liquid products resulting from pyrolysis leads to the minimal formation of char. However, the gas fraction (which could be used as a fuel) is composed mainly of CO, CO_2, H_2 and light hydrocarbons. The gas fraction obtained from the pyrolysis process is usually scrubbed to obtain the desired quality of the product, in terms of total hydrocarbon, soluble and particulate matter content. Hence, pyrolysis presents itself as a more sustainable option with a high recovery rate of products with a minimal contaminants discharge management.

Despite the growing spread of tyre incineration there is a general consensus that this technique causes hazardous pollutants emissions, due to the presence of primary contaminants and/or secondary precursors within the tyre material. Tyres also contain petrochemicals such as butadiene, styrene and benzene derivatives such as xylenes. Despite the high process efficiency of combustion, a small quantity of residual components can be detected in the combustion gas. Zinc is present in particularly high amounts since ZnO is used in the vulcanisation process. When co-incinerating tyres, an increase in the emission of heavy metals can be detected (up to 8% Hg and 9% Zn, Silva et al., 2009).

Pyrolysis also does not require any flue gas clean up as the flue gas produced is mostly treated prior to utilisation. It also provides an alternative solution to landfilling and reduces GHGs and CO_2 emissions. Pyrolysis in particular, and TCT in general, are sound solutions providing a more environmentally-friendly integrated system to recycle ELTs and recover valuable petrochemicals.

4.2. Prospects of End of Life Tyres Pyrolysis

4.2.1. Materials and Methods

Scrap tyre (ρ = 1.14 gm cc^{-1}) were secured from UMAC (Antwerp, Belgium) and tested isothermally (Ravago, Belgium), where ultimate analysis showed a high match with previous reports (Cunliffe and Williams, 1998; 1999; Berrueco et al., 2005; Silva et al., 2009). In wt%, the ELT contained the following: 30% natural rubber (SMR-5CV), 30% styrene-butadiene-rubber (SBR), 29% carbon black, 0.6% steric acid ($C_{18}H_{36}O_2$), 2.9% zinc oxide softener (ZnO), 0.9% S, 2.4% phenolic resin and 2.4% aromatic oil. The experiments were conducted by Ravago Plastics Co. (Belgium) and weight fractions of end of life tyres (x_{ELT}), as well as the weight fractions of lumped products (gases (x_g), aromatics (x_a), liquids (x_l) and char (x_c) were provided by the company as a function of time (s). The reported end of life tyres and products final fractions are the averaged value of conducting each experimental run three times by the company.

4.2.2. Isothermal Runs and Products Distribution

Previous reports on ELTs thermogravimetry show a typical derivative thermogravimetric curve with three decomposition steps: (i) decomposition of oils, plasticisers and additives between 200-325°C, (ii) polyisoprene (natural rubber) decomposition around 325-400°C, and finally (iii) at 400-500°C polybutadiene and SBR react (Senneca et al., 1999).

A pre-set temperature of 500°C was set to enable the decomposition of both polybutadiene (PBD) and polyisoprene (PI), with 15 mg (milled to below 0.1 mm to avoid mass and heat transfer resistance) of the sample being introduced into the thermobalance in order to conduct the TGA (Ravago Plastic Co., Belgium). Product analysis was carried out by means of a Hewlett Packard 6890 chromatograph provided with a thermal conductivity (TCD) and flame ionization detectors (FID) which were connected online to the balance by means of a thermostated line. Lumped product identification was carried out by means of a mass spectrometer (Shimadzu GCMS-QP20 I OS), and 99.9% pure nitrogen was used in the pyrolysis process. The pyrolysis products were grouped into rich gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char.

The main focus of ELTs pyrolysis and the gasification has always been maximizing the yields of gas products (Conesa et al., 2000; Berrueco et al., 2005). The final gas fraction in this process was evaluated at 0.02 wt%, which is what is found in many industrial pyrolysis processes. Maximum liquid condensate, measuring around 0.3% at the end of the run, was obtained (Figure 4.1).

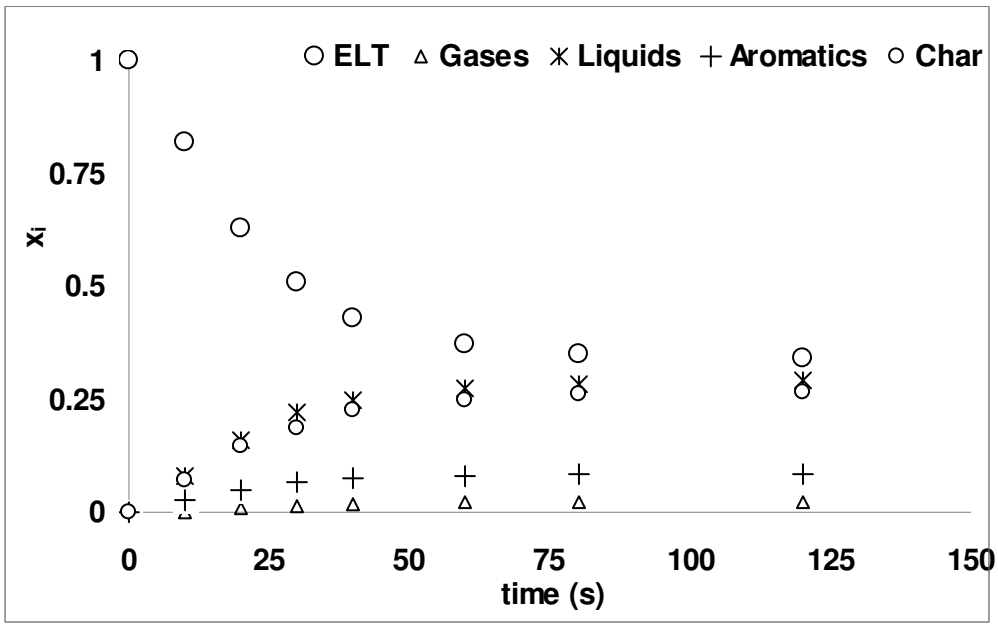

Figure 4.1 – Products collected experimentally for ELT as a function of time (s).

The main objective of the thermogravimetry was to obtain information about the thermal decomposition process of the tyre material and to compare it with previous isothermal reports found in the literature. Previous reports (Berrueco et al., 2005) show that a temperature of 500°C was not reached via classical TGA experimentation, whilst in this work isothermal pyrolysis with a preset temperature of 500°C was optimal for ELTs decomposition, thus simulating pyrolysis and co-pyrolysis of industrial flash units. Another observed aspect in this

work was the residual amount of the original ELTs (i.e. residual char), which was measured at 34% (metal and textile free), which is in agreement with previously published results (Conesa et al., 2000). Designing an industrial unit requires an understanding of the treated materials behaviour, and micro systems are seen fit according to a number of researchers in the field to determine weight loss kinetics (Roy et al., 1999; Conesa et al., 2000; Galvagno et al., 2002; Berrueco et al., 2005). It is imperative to have a proper scale-up of the process in order to establish a viable industrial design; yet a full product analysis is essential to understand the system's behaviour under certain conditions. Integrating a pyrolysis unit in an industrial scheme requires utilities (oil, gas and electricity) to be secured, as well as a sound model that will predict residue amounts, products and the heat and energy balance.

4.3. A Novel Approach in the Thermal Cracking Kinetics of Polyisoprene and Styrene-Butadiene Rubber

Equation 4.1 illustrates the thermal cracking mechanism proposed. The reactions are assumed to be irreversible, with the primary reaction being of a reaction order n.

$$(\mathrm{ELT}) \xrightarrow{k_1} (\mathrm{G}) \begin{bmatrix} \xrightarrow{k_2} (\mathrm{L}) \\ \xrightarrow{k_3} (\mathrm{A}) \\ \xrightarrow{k_4} (\mathrm{C}) \end{bmatrix} (\mathrm{L}) \xrightarrow{k_5} \mathrm{A} \qquad (4.1)$$

where ELT, G, L, A and C represent the fractions of ELT, gases, liquids, aromatics and char fractions, respectively, k_1, k_2, k_3, k_4, and k_5, respectively stand for the kinetic rate constant (s^{-1}) of the thermal degradation (primary reaction): ELT to gases, (secondary reactions): gases to, liquids, aromatics and char, (tertiary reaction): liquids to aromatics.

Where previous thermal cracking models are based on radical concentration estimations (McCaffrey et al., 1995; 1999), the model proposed in this work is based on lumped product analysis, facilitating schemes for industrial pyrolysis units and providing an engineering approach for the concerned industry.

The thermal cracking model shows n^{th} order primary cracking reaction (simplified in the previous equation) from ELTs to gases and the secondary reactions of gases to liquids, aromatics and char, and the tertiary side reaction of liquids to aromatics. The mathematical breakdown of the thermal cracking scheme of reactions is shown in the Equations 4.2-4.6:

$$dx_{ELT}/dt = -k_1 \, x_{ELT}^{n} \tag{4.2}$$

$$dx_g/dt = k_1 x_{ELT}^{n} - (k_2 x_1 + k_3 x_a + k_4 x_c) \tag{4.3}$$

$$dx_l/dt = k_2 x_g - k_5 x_L \tag{4.4}$$

$$dx_a/dt = k_3 x_g + k_5 x_1 \tag{4.5}$$

$$dx_C/dt = k_4 x_g \tag{4.6}$$

where k_1, k_2, k_3, k_4, k_5, correspond to the respective kinetic rate constants of (i) primary reactions of ELTs to gases and (ii) secondary reactions of gases to liquids, aromatics, char; (iii) tertiary reactions of liquids to aromatics. Fractions of ELT, aromatics, liquids, char and gases, are given as x_{ELT}, x_a, x_l, x_c and x_g, respectively. In mathematical terms, the optimisation problem is posed in Matlab as follows:

$$\text{Objective Function (O.F.)} = \min \sum_{i=1}^{N} \left| \frac{x_{ELT\,(exp)} - x_{ELT\,(th)}}{x_{ELT\,(exp)}} \right| \tag{4.7}$$

subject to

$$k_i \geq 0 \tag{4.8}$$

$$t_o = 0 \tag{4.9}$$

$$x_{ELT1}(t_o) = 1 \tag{4.10}$$

$$x_{g_0}(t_o) = x_1(t_o) = x_a(t_o) = x_c(t_o) = 0 \tag{4.11}$$

$$x_i(t_i) \geq x_{i-1} \tag{4.12}$$

where N is the number of time steps between initial reaction time (t_o) and final reaction time (t_f), $x_{ELT(exp)}$ is the experimental end of life tyre (ELT) fraction, $x_{ELT(th)}$ is the theoretical ELT fraction resulting from the set of differential equations (4.2.-4.6.), k_i are the kinetic rate constant

of the differential equations and are determined with the reaction order (n) by the software Matlab using built-in functions (Fminsearch) and (ODE 45), $x_{ELT}(t_o)$ is the ELT fraction at time equal to zero (start of reaction), x_i is the product fraction at time equal to or greater to zero. The objective function is set as the sum of error between the experimental and theoretical polymer fractions. Equations (4.8-4.12) represent the optimisation bounds for the kinetic rate constants, initial reaction time, ELT and products fractions, respectively. The product fractions are calculated as a function of the rate equations, resulting in the highest regression coefficients (see Appendix A).

The model was solved using Matlab software (version 7.6 2008) by applying the 4th order Runge-Kutta (RK) method. To represent the ELT fraction (x_{ELT}) throughout the reaction time, a theoretical fit was used. The absolute error between the theoretical fit and the software solution was minimized as an objective function using ODE-45 method in Matlab, resulting in the highest possible regression coefficient (R^2) (see Annex A and B). The software will output the optimized kinetic rate constants (k_1-k_5) and the reaction order (n). A similar approach was undertaken in Chapter 3 for the polyolefins studied.

Equations (4.2-4.6) permit the evaluations of the reaction order (n) of the ELTs degradation, which was found to be equal to 1.4. The secondary and tertiary reactions are assumed to be of order 1, and the kinetic rate constants (k_i) were evaluated and are shown in Table 4.1.

Table 4.1 Results summary of the depolymerization rxns of studied ELT in isothermal pyrolysis (500^{o}C), showing kinetic rate constants (s^{-1}) of single path reactions (k_i) and overall rate constant (k_o).

Material	T (^{o}C)	$k_1 \approx k_o$	k_2	k_3	k_4	k_5
ELT	500	0.011	0.009	0.0002	0.0049	0.0009

Previous work by Chen et al. (2001) demonstrated the applicability of an nth order model to produce volatiles (See section 2.10.). Their work showed a range of n = 1.63 – 1.98, depending on the grade of the tyre. They also compared their work with Conesa et al. (2000) who developed a first order model for the pyrolysis of tyres. In this work, the order of the reaction was set to be solved in the model and resulted in n = 1.4.

Generally, ELTs degrade whilst the products are formed, and the gases production pattern reached a peak point, when the ELTs started to demonstrate a degradation pattern. This is the point where the products are more dependent on the gas collected (intermediate) stage, as described in the model mechanism. Prior to this point, the char, liquids and aromatics are produced with less rapidity (Figure 4.2). The model accounts for the residual tyres (x_{ELT}) fraction, as well as the products yielded by the pyrolysis reaction.

The gases reached a peak point after 88 s, when they started to decrease again with a final gas fraction (x_g) of 0.43. The final char experimental value was estimated at 0.26. However, the model predicted a char value of 0.21, resulting in a 19% error. The error between the experimental (x_l = 0.39) and model (x_g = 0.31) values of liquid fraction was estimated as 20%. The error was estimated as 3% between the final experimental ELT fraction (x_{ELT} = 0.33) and the model value (x_{ELT} = 0.34). The model results and experimental values of end of life tyres fractions (x_{ELT}) were plotted against each other to look at the results compatibility. Figure 4.3 shows the model vs. experimental values for the ELT grade studied. It can be seen that the mid section of the reaction points were more scattered than the rest, and this deviation occurs as the products evolve until they reach their final state (at 120 s).

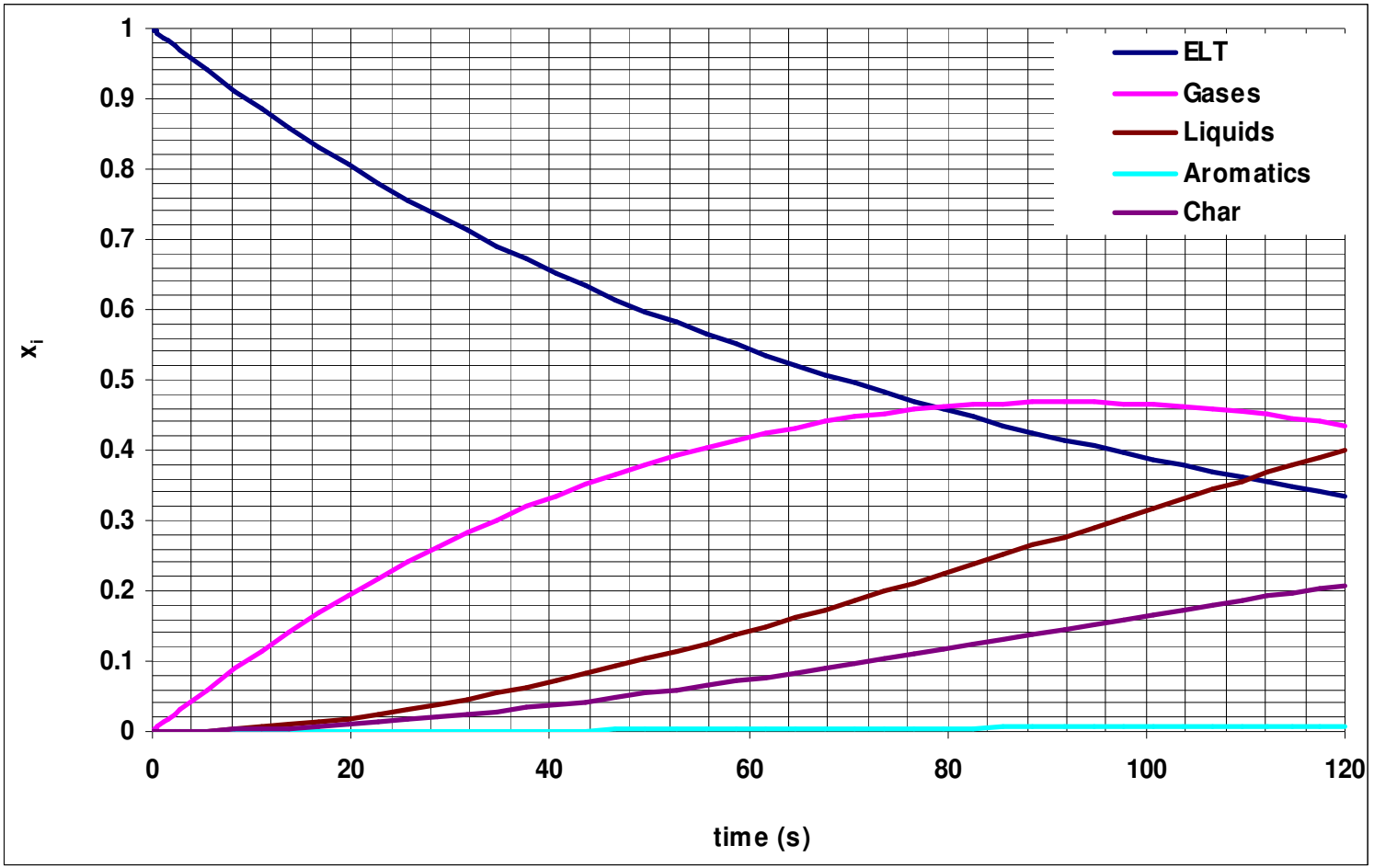

Figure 4.2 - Model result showing product formation and ELT loss as a function of reaction time (s) at *500* °C.

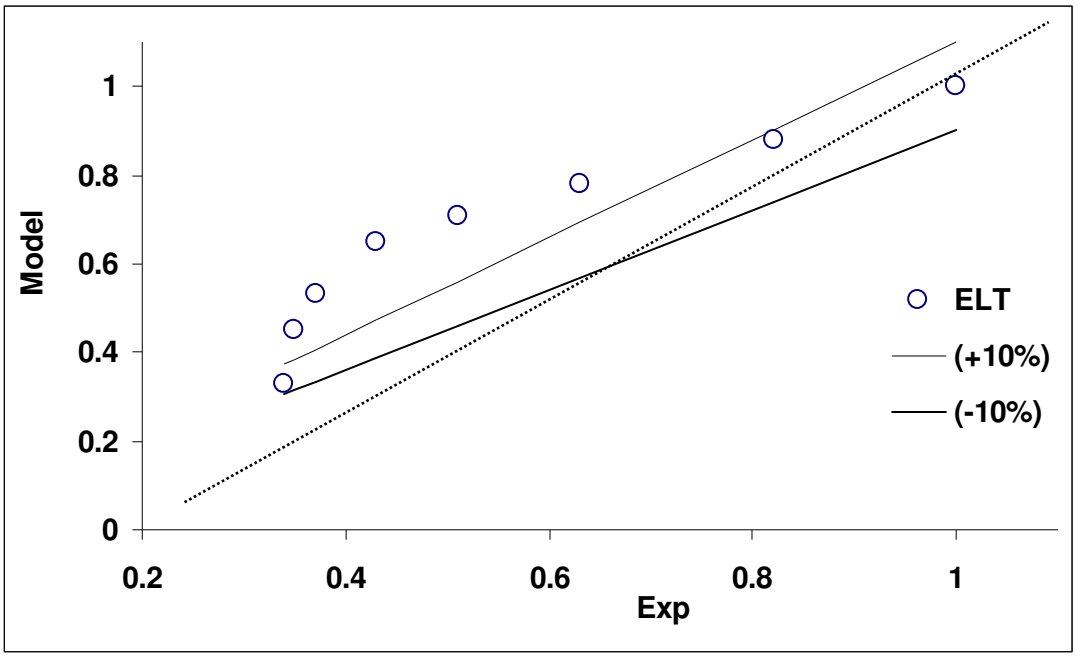

Figure 4.3 Model vs. experimental values for x_{ELT} at 500°C

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4.4. Concluding Remarks

Laboratory scale isothermal pyrolysis experiments on ELTs were conducted. Conversion time and product analysis proved the high potential for this method to be carried out in industrial units. A thermal cracking scheme was proposed based on the global yielded products, which were grouped into four categories, namely gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char. The evaluation of depolymerisation kinetics (from primary, secondary and tertiary reactions) showed a high match with the experimental results, resulting in an overall rate constant (k_o) of 0.011 (s^{-1}).

Results from this case study have demonstrated the potential for this scheme to be carried out in the future. Previous reports have focused solely on maximising gas yield, and differences and incoherence between previous reports are attributed to sample type and weight, operating conditions and the omission of heat and mass transfer, as well as the mode of pyrolysis.

Chapter 5

Literature Survey: Life Cycle Assessment Methodology

This chapter contains a review of life cycle assessment (LCA) and its standard methodology. Published reports on LCA and its application to thermo-chemical treatment (TCT) reactors, incineration units (IUs) and other thermal treatments are also presented. It also details different software packages used in performing LCA, in order to demonstrate the different capabilities of each.

Parts of this chapter were published in:

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**). Recycling and recovery routes of plastic solid waste (PSW): A review, *Waste Management*, **29(10)**; 2625-2643.

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**). The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, *Progress in Energy & Combustion Science*, **36(1)**; 103-129.

Al-Salem, S.M., Mechleri, E., Papageorgiou, L.G. and Lettieri, P. (**2012**). Life cycle assessment and optimization on the production of petrochemicals and energy from polymers for the Greater London Area, *Computer Aided Chemical Engineering,* **30(1)**, 101-106 & In: Proc of the 22nd European Symposium on Computer Aided Process Engineering (ESCAPE 22), Part A; Edited by: Bogle, D., Fairweather, M., pp. 101-106, Elsevier. London (*England*), UK, 17th-20th June.

5.1. Towards a More Sustainable Practice through Recognising Recovered Polymers as a Feedstock: Life Cycle Assessment Implementation

LCA, as defined by Garcia-Serna et al. (2007), is:

> '*a process to evaluate the environmental burdens associated with a product, process or an activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify opportunities to effect environmental improvements*'.

The applicability of LCA is twofold. Firstly, LCA can be used for the quantification and evaluation of the environmental performance of a product or a process and thereby aid decision makers on choosing amongst alternatives (Moberg et al., 2005; Garcia-Serna et al., 2007; Eriksson et al., 2007, Tarantini et al., 2009). Secondly, it provides an excellent knowledge base for engineers and environmental mangers in the assessment of potential improvements in the environmental performance of a system (Garcia-Serna et al., 2007).

In the following section, a brief history of LCA is given. The standardised methodology of LCA is also detailed with a review of the literature incorporating thermal treatments, recycling and polymer treatment processes. The results of each study are compiled and gaps in the published research are also indicated, as well as their relevance to the work conducted in this thesis.

5.2. Background, Definitions & Terminology

LCA is considered one of the best tools which can be implemented in eco-performances of design, processes, engineering solutions, waste management scenarios or disposal methods and systems. LCA is an objective methodology developed from chemical engineering principles and energy analysis, and is able to account for materials input, energy data, economical analysis and emissions related to the life cycle of a product, service or a process (Perugini et al., 2005). LCA accounts for every stage in the cycle of the product or service, from resource extraction (cradle) to the ultimate end-of-life treatment (grave), hence the term 'life cycle' is used. Recovery, disposal or production stages before the grave are typically referred to as gates.

Understanding the importance of LCA can be witnessed from its development throughout recent history. In the early 1960s, concerns about the rapid depletion of fossil fuel grew and this

sparked the interest in finding ways to account for energy use (Ho, 2011). The first LCA report was published by Harold Smith in 1963 at the World Energy Conference, where his calculations were concerned with the requirements for the production of chemical intermediates (Tsilingiridis et al., 2004). Later, two studies initiated the trend of predicting finite resources in the world. These were: *The Limits to Growth* by D.H. Meadows et al., which was first published in 1972 in the US by Potomac Associates (Washington DC); and *A Blueprint for Survival* by Edward Goldsmith and Robert Allen, which appeared as a special edition of The Ecologist and was published as a book in 1972 by Ecosystems Ltd (Ho, 2011). The Coca-Cola® Company conducted a LCA study on different beverage containers in 1969, and between the years 1970-1975, the United States Environmental Protection Agency (USEPA) refined their methodology and created the resource and environmental profile analysis. More recently, the International Standardisation Organisation (ISO) developed the LCA standards between the years 1997-2006.

The continued development of recycling and recovery technologies, investment in infrastructure, the establishment of viable markets and participation by industry, government and consumers, are all considered priorities of the highest order (Scheirs, 1998). Today, 90% of plastics used are synthesised using non-renewable fossil resources. Therefore, it is essential to integrate waste management schemes into the production cycle of plastics and treatment schemes of PSW. Whilst recycling is considered a sustainable practice, implying an integrated waste management (IWM) scheme provides a more sustainable use of energy and supplies (Figure 5.1).

LCA schemes aid in the selection and application of suitable techniques, technologies and management programmes to achieve specific waste management objectives and goals. The target of IWM is to control the waste generation from processes to meet the needs of a society with minimal environmental impact and with efficient resource usage by activating the potentials of waste prevention, re-use and recycling. The IWM cycle can be sub-divided into six categories, namely: (i) waste generation, (ii) waste handling, sorting and processing at the source, (iii) collection, (iv) separation and processing, (v) transfer station handling and waste transport, and finally (vi) disposal. These functional groups are paramount, since they enable a framework to be developed and defined for evaluating the impacts of the proposed changes in solid waste functions (Al-Jayyousi, 2001).

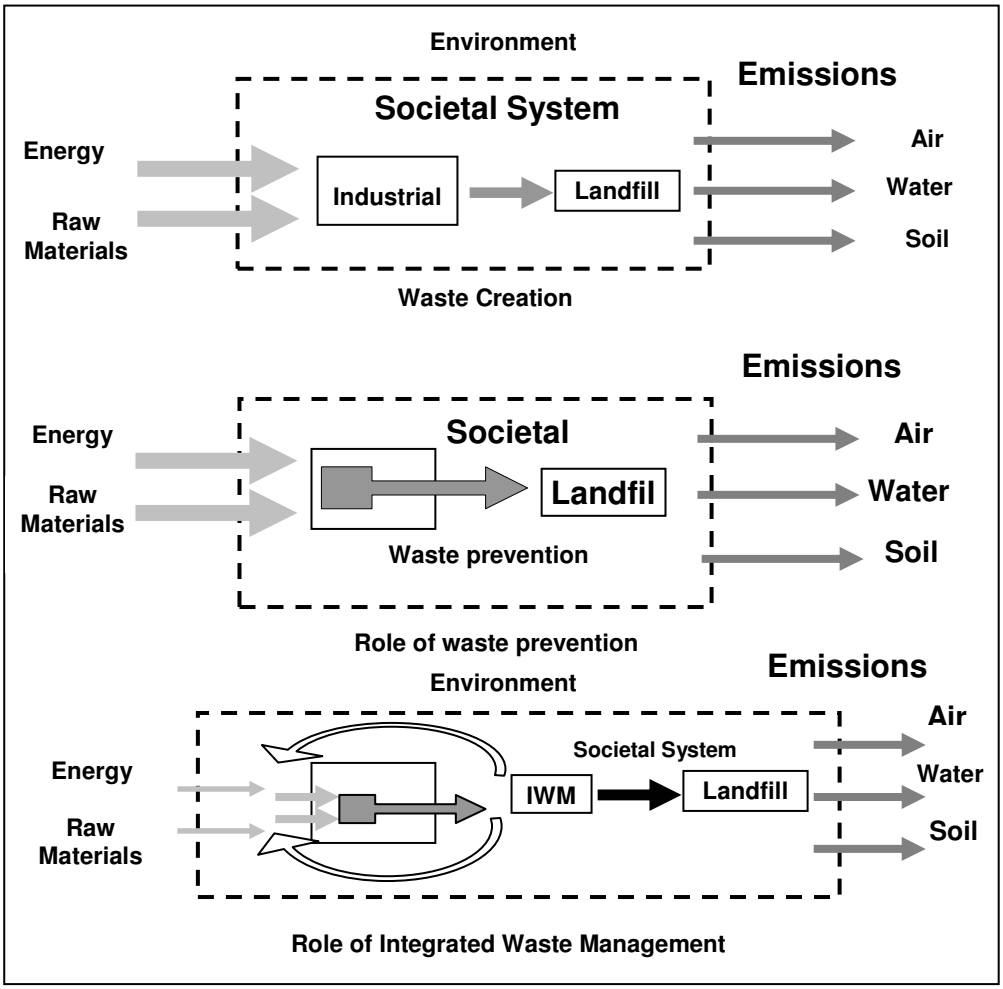

Figure 5.1 - Respective roles of waste prevention and integrated waste management.
Source: Kirkby et al., 2004.
Note: In Life Cycle Assessment (LCA) studies, a 'system' is defined (with boundaries indicated by broken lines). Energy and raw materials from the 'environment' are used in the system. Emissions, including solid waste, leave the system and enter the environment. Waste prevention includes the role of cleaner production, innovative services, sustainable consumption and prevention by design.

5.3. Life Cycle Assessment Methodology

ISO methodology and standards state that the LCA structure consists of four very distinct phases, which together contribute to an integrated approach to waste management (ISO, 2006, Figure 5.2). These phases are (in consequential order): (i) goal and scope definition; (ii) life cycle inventory (LCI) or inventory analysis; (iii) life cycle impact assessment (LCIA) or impact assessment, and finally; (iv) interpretation.

Goal and scope definition defines the extent and scope of the study, and most importantly its boundaries. It is essential to define why a LCA is to be carried out and what decision is to be informed by the results (Clift et al., 2000). Goal and scope definition is considered a very important element for the interested audience, describing the system studied as well as the options that will be compared (e.g. scenarios). The scope of the study is expressed in terms of

the system boundaries and the processes and operations which are to be included.

LCAs are commonly carried out to compare a number of alternatives. The basis for comparison, common between all alternatives, is termed the functional unit (FU) of the study (Clift et al., 2000). It is paramount to distinguish between the 'foreground' system and the 'background' system. The former being a set of processes whose selection or mode of operation is affected directly by decisions based on the study (in this case waste management activities), whilst the latter is defined as all other processes that interact with the foreground system, usually by supplying or receiving materials and energy (Figure 5.3).

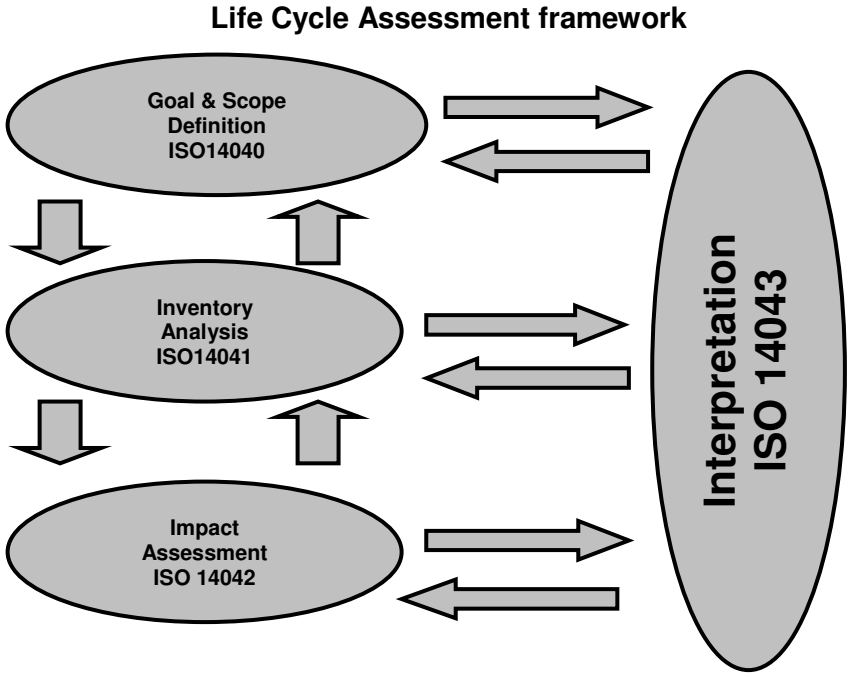

Figure 5.2 - Phases of Life Cycle Assessment (LCA) indicating guidelines and standards for each.

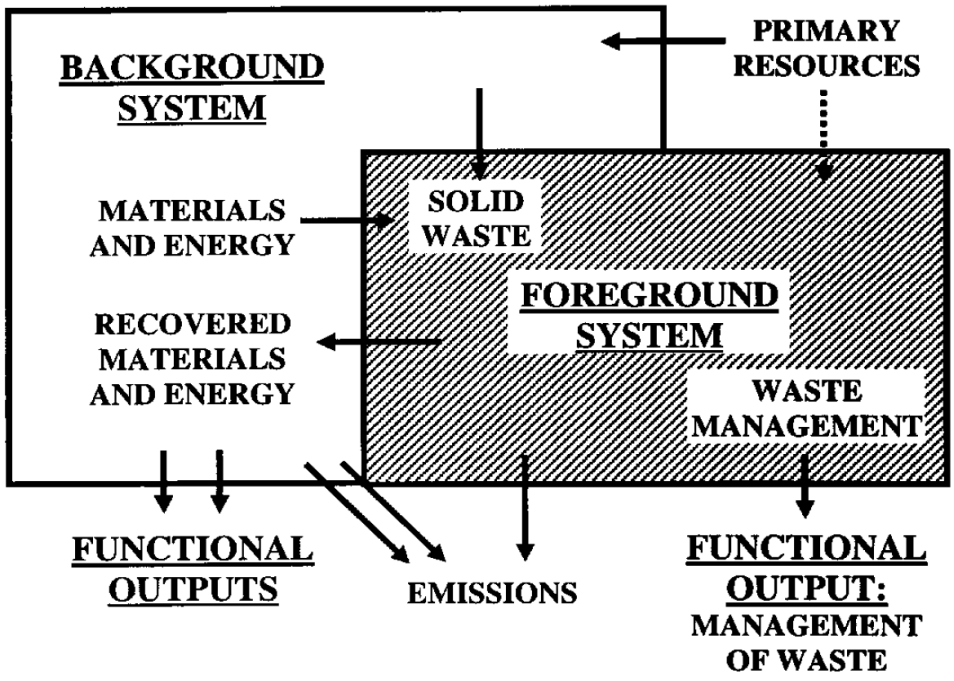

Figure 5.3 - Foreground and Background systems used explicitly by the EA (UK).
Source: Clift et al., 2000.

As for the LCI, many consider this to be the core of an LCA investigation. This stage collects all inputs of materials and energy that cross the boundary between the product and the service system over the whole life cycle. Environmental burden assessments and quantification fall within this stage. The recommended way to report a LCI for a waste management scheme, according to Clift et al. (2000), is: direct burdens plus indirect burdens minus avoided burdens. Direct burdens are those associated with the waste management operations themselves (arising in the foreground system), whilst indirect burdens are associated with providing materials and energy to the waste management operations, i.e. those arising in the supply chain of materials and energy provided to the foreground system. Avoided burdens are those associated with economic activities that are displaced by materials and/or energy recovered. However, since indirect and avoided burdens cannot normally be defined, their numerical estimates should be obtained from a reliable database (Perugini et al. 2005), and examples of these are the European Reference Life Cycle, SimaPro and the Gabi Software databases. In this thesis, the way to report LCI as recommended by Clift et al. (2000) has been employed (see Chapter 6).

In the LCIA stage, the main objective is to understand and evaluate the magnitude of the potential environmental impacts of a given system. This stage organises the LCI inputs and outputs into specific selected impact categories and models the inputs and outputs for each category into an aggregate indicator (Udo de Haes and Lindeijer, 2002). The final stage of a LCA is the interpretation stage, which involves all of the phases in the LCA process and reporting them accordingly.

A LCIA incorporates impacts and environmental burdens of the different stages of the life cycle. Two main categories fall under the remit of environmental impacts: depletion and pollution impacts. Depletion impacts include abiotic resource depletion (use of renewable and non-renewable resources, e.g. wind, water, etc.) and biotic resource depletion (use of natural resources, e.g. biosphere, forests, coal petroleum, etc.). Regarding the pollution impact category, this includes: ozone depletion, human toxicity, smog formation, acidification and global warming potentials, eutrophication, etc. Table 5.1 shows a number of quantification methods for the main burdens which are typically used in LCIA.

Table 5.1 Typical life cycle impact assessment (LCIA) categories and their quantification methods.

Impact Category	Definition	Quantification Methods	Notes	Reference
Ozone Depletion Index (ODI)	The final sum of chemicals characterised with respect to their ODP_i.	$ODI = \sum_i (e_i \times ODP_i)$ (5.1) where e_i is the emission (Kg) of substance i and ODP_i is the ozone depleting potential of substance i.	Much of ODIs were stressed after the initial Montreal protocol entry in 1987.	Bare et al. (2003).
Global Warming Index (GWI)	This category refers to the potential change in the earth's climate caused by the build-up of (GHGs).	$GWI = \sum_i (e_i \times GWP_i)$ (5.2) where e_i is the emission (Kg) of substance *i* and GWP_i is the global warming potential of substance *i*.	In this work, the Gabi 5 Database (DB) was used for the IU GWP calculation.	Bare et al. (2003); Johnke (2000); USEPA, (2001).
Energy credit/Total CO_2 emission	This refers to CO_2 emission calculation with regards to energy credits in a unit operation, typically an incinerator	$Emission_{Corr} = TE_{i,cCorr} - usable/used\,energy \times EF_{PPMix}$ (5.3) $TE_{CO2-eq} = Emission_{Corr} \times GWP_i$ (5.4) where $Emission_{corr}$ is the corresponding emission of substance i (tonne), usable/used energy is the energy consumption or production of the unit (kWh) and EF_{PPMIX} is the emission factor of power plant mixtures for substance i (tonne).	Assumptions could be found in indicated reference.	Johnke (2000)
Acidification Potential (AP)	The process whereby air pollutants, mainly NH_3, SO_2 and NO_x, are converted into acidic substances.	$AP = \sum_{i=1}^{n} ec_i \times B_i$ (5.5) Where ec_j represents the AP of substance i expressed relative to the value for SO_2 and B_i is the emission (Kg) of substance *i*.	For the case relevant to incineration of MSW, power plant mixtures could be used. See Johnke (2000); IPCC, (2006a, 2006b).	Azapagic et al. (2004)

Table 5.1 (cont'd) Typical life cycle impact assessment (LCIA) categories and their quantification methods.

Ecological Toxicity Potential (ETP)	Quantitative measure that expresses the potential ecological harm of substances released into the surrounding environment.	$CSR_i^{nm} = \frac{PEC_i^m}{S_i^n}$ (5.6) $ICR_i^m = \frac{FA^*}{C_i^n}$ (5.7) $ETP_i^{nm} = \frac{[CSR_i^{nm} \times ICR_i^m]}{[CSR_x^{nm} \times ICR_x^m]}$ (5.8) $ETP_i^{air}(\text{overall}) = [0.5 \times ETP_i^{air,soil}] + [0.5 \times ETP_i^{air,sw}]$ (5.9) $ETP_i^{sw}(\text{overall}) = [0.5 \times ETP_i^{sw,soil}] + [0.5 \times ETP_i^{sw,sw}]$ (5.10) where ETP_i^{nm} is the ecotoxicity potential, CSR_i^{nm} is the concentration (mol/m³) of chemical i to source ratio in medium m based on a unit release (mol/m³) to compartment n, ICR_i^m is the impact to concentration ratio for chemical i in m, which is the measure of potential impact.	PEC_i^m is considered the predicted environmental concentration of chemical i. Whilst, FA^* is the standard measure of harm, and C_i^n is the benchmark concentration for chemical i.	Hauschild and Pennington, (2002); Bare et al. (2003).
Fossil Fuel Index (FFI)	An assessment of fossil fuel in a quantitative way	$FFI = \sum_i (N_i \times F_i)$ (5.11) Where N_i is the increase in energy input requirements per unit of fuel consumption of fuel i and F_i is the consumption of fuel i per product unit.	-	Geodkoop and Spriensma, (1999).

5.3.1. System Expansion and Problems Arising from Allocation

System boundaries in Life Cycle Assessment (LCA) studies should always be clearly indicated. Inputs and outputs to the system are followed from 'cradle' to 'gate' or 'grave', and hence inputs are flows drawn from the environment and outputs are flows discarded to the environment (Finnveden, 1999; Ekvall et al., 2007). Both inputs and outputs should not have any human transformation affecting them. As previously discussed, a LCI is the phase of a LCA where energy and material flows are compiled and quantified and this is considered the core of a LCA investigation. However, an allocation problem (as it is commonly referred to) arises when a multifunction[1] process is defined. Allocation problems can be classed as either methodological or open-loop recycling (Ekvall and Finnveden, 2001).

Methodological allocation problems arise in a LCI when a multifunctional process fulfils one or more functions for the products life cycle, whilst also fulfilling another function for another product's life cycle. The problem is in deciding what share of the environmental burden should be allocated to each process investigated. The second type of allocation problems occurs in open-loop recycling, i.e. when a material from one product is recycled into another. Here, the main life cycle fulfils a function in the life cycles of two products (Ekvall and Finnveden, 2001). According to ISO 14041, allocation should be avoided through the division of the multifunction process or through system boundary expansion (Ekvall and Finnveden, 2001), with the latter being the more preferable option since it reflects the full life cycle of the product in a more realistic manner. System expansion is also a very adequate way in which to avoid allocation as long as data can be obtained for the alternative production or processing method (Ekvall and Finnveden, 2001). Finnveden (1999) addressed the issue of system boundary expansion to include several functions. Typically, different processes provide different functions and comparisons between the two would be difficult. Two methods are reported here to avoid the allocation problem by system expansion.

The first method of comparison between two processes is to add the equivalent amount of product to one of the processes, and thus it is possible to compare the two processes. The second method is to subtract the product using an alternative method (i.e. off-setting). In this method, avoided emissions will occur and environmental interventions may be negative, and in such reports, the system is said to be *credited* with an equivalent amount of product (e.g. heat, electricity, etc.) being produced in an alternative manner (Finnveden, 1999). In fact, the input material to a life cycle can either be sent to landfill or re-enter further life cycles as a substitute for virgin materials. Substitution means avoidance of products manufactured from primary resources through secondary materials gathered from recovery and recycling. In other terms, the

[1] A multifunctional process is an activity that fulfils more than one function simultaneously (Ekvall and Finnveden, 2001).

production of a recycled material that re-enters further life cycles represents a potential credit for avoiding the production of an equivalent quantity of virgin products (Blengini et al., 2012).

Finnveden (1999) also discussed in detail the drawbacks of using system boundary expansion, which can be summarised as follows:

- The models get larger and more complicated. Models used in system expansion are often based on several critical assumptions concerning materials and energy sources being replaced.

- Loss of transparency. This is the case when subtracted systems are used and the avoided function were not adequately described and justified.

- Loss of the capability of studying one product in isolation, since it is now part of an expanded system.

Finnveden (1999) also addressed the issue of 'identical' products in LCA systems. Identical products in a LCA context, does not mean that they have to be exactly identical in all aspects. It is sufficient simply if the products are providing a comparable function to a user or if they have the same environmental impacts, in which case the products can be disregarded. If the products are not providing comparable functions, then they cannot replace each other. If the products do not have the same environmental impacts, then at least the differences should be included in the LCA.

In this thesis, the system expansion methodology to credit all potential products as described by Finnveden (1999) is used in Chapter 6. The attributional life cycle assessment (ALCA) study performed on the greater London area (GLA) considers the production of a number of valuable petrochemicals and energy from different technologies and processes. The petrochemicals, products and energy resulting from each scenario were off-set against conventional production methods (see Chapter 6). Off-setting the produced energy and products from the integrated scenarios avoids the allocation problem that could result from introducing a TCT unit to the baseline scenario (i.e. Scenario 1, see Chapter 6). The polymeric fraction introduced into the TCT reactors fulfils two functions simultaneously; it is the product from the MRF and the feed to either a pyrolysis reactor or a hydrocracking unit. Consequently, a multifunctional FU problem can be avoided by system expansion in this case (which was done in Chapter 6).

System expansion also makes it possible to compare between the scenarios in a systematic approach, reflecting the full life cycle of the FU (Finnveden, 1999; Ekvall and Finnveden, 2001; Valerio 2009, Rigamonti et al., 2009). In addition, average and marginal electricity data can be

used to off-set the production of electricity. Average data typically reflects the current situation of the studied boundary. In contrast, marginal effects data are the consequences of infinitesimal or small changes in the volume produced of a good (Eriksson et al., 2007). Marginal effects data used include nuclear, wind, hard coal or natural gas energy production on a standalone basis. The UK combined cycle gas turbine (CCGT) heat generation data were used to off-set the heat production from the IU with CHP (see Chapter 6). Off-setting the energy produced against average and marginal data provides a realistic overview of the LCA performed, since it considers the UK national grid and other marginal sources that exist in this country. Sections 5.5-5.6 summarise LCA studies addressing the system expansion concept (for avoiding allocation problems), avoided burdens and the thermal treatment of polymers in the urban environment.

5.3.2. Hot Spot Analysis in LCA Studies

Another concept commonly addressed by LCA studies is hot spot analysis (HSA). HSA is used to define the unit operations within a plant, process or activity that contribute to high emissions or environmental indicators in general (Patel et al., 2012). HSA can be performed on processes within a system or in a deeper manner going into the individual contributions of the different activities within a process.

Chaya and Gheewala (2007) performed a LCA on two MSW to energy schemes undertaken in Thailand; incineration and anaerobic digestion (AD). The FU considered was one tonne of MSW which would be treated either by an incinerator with a 250 tpa capacity or an anaerobic digester with a 50 tpa capacity. Credits were provided to the incineration scheme for avoided electricity production, and to the AD for avoided electricity and fertilizer production. Data included in the study were obtained from a number of sources including the SimaPro 5 software database and governmental databases. The study showed that the AD (-276 kg CO_2-eq) was preferable to incineration (273 kg CO_2-eq) in terms of global warming potential (GWP). AD was also preferable to incineration in terms of acidification potential (AP), which was estimated at 2.37 kg SO_2-eq for incineration and -1.57 kg SO_2-eq for AD. This was partly because more than 60% of the waste was biodegradable and thus suitable for AD. There were a number of hot spots identified in both schemes that could be improved, such as the lime production in the IU which contributed to the majority of the studied impacts. Replacing lime by other materials or methods that contribute to a smaller impact was recommended. For AD, nutrient enrichment processing was identified as a hotspot due to emissions into water.

Patel et al. (2012) performed a LCA to identify if solid recovered fuel (SRF) plants at scales of 50 and 100 ktpa incorporating fluidized bed combustion (FBC) technology were environmentally friendly. The system boundary included power production, collection of the

MSW, pre-treatment of the MSW, the Fairport process for SRF production, pelletisation, transportation of the SRF to the power generating facility, storage of the SRF, storage of bottom ash, transportation of bottom ash to be used as secondary aggregate, and transportation of fly ash to a specialised landfill site. The HSA revealed that the most polluting units in the SRF plant arose from the energy production sub-system, specifically the combustor and boiler, with the combustor releasing twice as much as the boiler at7503 kg CO_2/h and 3652 kg CO_2/h, respectively. Blengini et al., (2012) studied the thermal treatment (as a recycling process implementing a furnace with a foaming process) of recycled foam glass in Italy. The three scenarios compared depended on the mixing ratio between soda lime glass and special glass. Scenario 1, 2 and 3 contained the following percentage of soda lime glass: 50%, 80% and 20%, respectively. System expansion was implemented in the study, thus net environmental gains relevant to glass and ceramic fragments/powders recovery, metal scrap recycling, plastic scrap energy recovery and landfill avoidance were allocated to recycled foam glass. Consequently, the adopted FU was 1 tonne of recycled foam glass aggregate. The results, normalised to the highest impact scenario, indicated that scenario 2 had the lowest gross energy requirement which was estimated at about 85%, whilst scenarios 1 and 3 resulted in a normalised estimate of 93% and 100%, respectively. In contrast, the GWP (kg CO_2-eq) of scenario 2 was normalised as 100%, whilst scenarios 1 and 3 resulted in an estimate of 93% and 96%, respectively. The energy use for the thermal process was determined to be a hot spot and the LCA results suggested switching to a natural gas powered kiln or an electric kiln powered with a natural gas co-generator, the latter being the solution adopted by the industrial partner of this study's authors.

5.4. Types of LCA Studies: Does it Matter to Distinguish between the Different Types of LCA Conducted?

LCA studies can be classified as either a consequential LCA (CLCA) or an ALCA (Brander et al., 2008). Policies such as the UK's renewable transport fuel obligation and the EU's renewable energy directive have been criticised for failing to distinguish between the two types (Brander et al., 2008) and this can lead to:

1. Applying the wrong method to the case in hand.
2. A combination of the two methods within a single analysis.
3. A misinterpretation of the results obtained.
4. An unfair comparison of the results derived from different methods.

ALCA is concerned with describing the environmentally relevant physical flows to/from a life cycle and its sub-systems. It ideally includes average data on the unit processes (Eriksson et

al., 2007). ALCA provides information regarding the impacts of the processes used to produce a certain product and also includes the consumption and disposal of said product (Brander et al., 2008). However, this type of study does not consider indirect effects arising from changes in the output of a product. ALCA is used to identify direct impacts within different parts of the life cycle. An overview of the main differences between the two types of LCA is given in Table 5.2. The LCA conducted in this work is of the attributional type. Energy requirements, production of chemicals and petrochemicals, recovery of power and heat and material flows of the system boundary were accounted for and are reported in Chapter 6.

Table 5.2 Main differences between Attributional LCA (ALCA) and Consequential LCA (CLCA). Source: Brander et al. (2008)

	ALCA	CLCA
Definition (Eriksson et al., 2007)	A methodology for life cycle inventory (LCI) analysis aims at describing the environmentally relevant physical flows to and from a life cycle and its subsystems.	A methodology for describing how the environmentally relevant physical flows to and from the technosphere[1] will change in response to possible changes in the life cycle.
The study includes (Eriksson et al., 2007)	It ideally includes average data on the unit processes.	It includes unit processes that are significantly affected whether they are inside or outside the life cycle. It ideally includes marginal data on bulk production processes in the background system.
Questions the method aims to answer	What are the: i. total emissions from the processes ii. material flows directly used in the life cycle of a product	What are the changes in total emissions as a result of a marginal change in the production (and consumption and disposal) of a product.
Application	Understanding the emissions directly associated with the life cycle of a product. Also appropriate for consumption-based emission.	Applicable for informing consumers and policy-makers on the change in total emissions from a purchasing or policy decision.
Not appropriate for	Quantifying the change in total emissions resulting from policies that change the output of certain products	Consumption-based emissions accounting.
System boundary	The processes and material flows directly used in the production, consumption and disposal of the product.	All processes and material flows which are directly or indirectly affected by a marginal change in the output of a product (*e.g.* through market effects, substitution, use of constrained resources *etc.*).

Table 5.2 (Cont'd) Main differences between Attributional LCA (ALCA) and Consequential LCA (CLCA). Source: Brander et al. (2008)

Uncertainty	Low uncertainty because the relationships between inputs and outputs are generally stoichiometric	Highly uncertain because it relies on models that seek to represent complex socio-economic systems that include feedback loops and random elements

[1]The part of the physical environment affected through building or modification by humans

5.5. Application of Software and Simulation Environments in Life Cycle Assessment Studies

In several countries, LCAs have been carried out to compare environmental impacts of applied waste management system strategies. Several computer aided solutions are currently available in the market, most of which are designed for end-point analysis, i.e. at the end of the process design (Garcia-Serna et al., 2007). These software packages provide the user with an environment in which processes can be simulated and data inputted to produce compiled results reports that follows the different stages of the life cycle. Examples of such software packages used in LCA methodology are SimaPro (Pre Consultants), Umberto (IFU Hamburg and IFEU Heidelberg) and Gabi (Department of Life Cycle Engineering at the University of Stuttgart and PE International GmbH). These software packages are based on the ISO 14040 methodology and all implement a number of databases (Pieragostini et al., 2012), such as, ECOINVENT database (Swiss Centre for Life Cycle Inventories). Table 5.3 contains a list of the most common software packages available together with a brief description of each package.

The commercial WISARD (Waste Integrated System Assessment for Recovery and Disposal) LCA tool was developed in France by the Ecoblian Group. De Feo and Malvano (2009) used this particular tool in their study, which focused on the environmental impacts produced by MSW systems in Campania, a region in southern Italy. Twelve scenarios were considered, of which the first ten were based on a separated kerbside collection of paper and cardboard and dry residue. Scenario 11 was based on a combined kerbside collection of plastics (14% of total waste) and metals, and in scenario12 on a bring collection of glass, although scenarios 11 and 12 didn't consider the thermal treatment of dry residues. The impact assessment categories evaluated were as follows: renewable energy use, non-renewable energy use, total energy use, water, suspended solids and oxydable matters index, mineral and quarried matters, GHGs, acidification, eutrophication, hazardous waste, non hazardous waste. The study indicated that metals and plastics treated after collection with no RDF incineration was not the most environmentally sound option for renewable energy use, total energy use, water, suspended solids and oxydable matters index, eutrophication, and hazardous waste.

Table 5.3 LCA software packages commonly used and available on the market.
Source: Garcia-Serna et al., (2007)

Software	Description	Company
LCA	LCA systematically describes and assess all flows to and from nature in a cradle to grave fashion. It is used commonly with life cycle analysis or Ecobalance studies.	PER
SimaPro	The SimaPro family (different versions) allows the users to implement LCA in a flexible way. The user can collect, analyze and monitor the environmental performance of processes. The user can model LCA in a systematic way following the ISO 14040 recommendations.	PER
Umberto	This software visualizes material and energy flows. It can model complex structure with its graphic interface. It can also model production facilities in a company, processes and value chains.	German ifu Hamburg GmbH in cooperation with Ifeu
Software Development Life Cycle (SDLC)	This package is also known as a linear sequential model, where activities such as system/information engineering are modelled.	Stylus Systems Inc.
ECO-it	This software allows you to model a complex product and its life cycle in a short period of time. It calculates the environmental burdens, and shows which part contributes most. Hence it is ideal for Hotspot Analysis (HSA).	PER
Gabi	This software provides solutions for different problems regarding cost, environment, social and technical criteria, optimization of processes and manages external representation in these fields.	PE Europe (University of Stuttgart)

The WISARD software was also used by Buttol et al. (2007) to compare three different scenarios of waste management in the district of Bologna, Italy, which included: waste collection, transportation, sorting, recycling, composting, incineration and landfilling. The three scenarios built using the software incinerated different amounts of collected waste (30%, 50% and 37%, respectively), and the main findings of the study can be summarised as follows:

- In all scenarios, recycling was confirmed to save energy (by 3 to 5 times) when compared to landfilling.
- In all scenarios, recycling emits the lowest level of volatile organic compounds.
- Scenario 3 produced the lowest avoided impact of toxic compounds, expressed as 1-4 dichlorobenzene-eq (1,4 DCB-eq).

The Gabi software was used to model the waste management system of Prato, Italy by Tarantini et al. (2009). The study included five indicators: non-renewable primary energy, GWP, eutrophication potential, photochemical ozone depletion potential and environmental/human toxicity potential. The system modelled included RDF sent to an IU with CHP, organics sent to composting, metals recycling, mixed waste compounds landfilling and biogas recovery. The best performance in terms of avoided impact was obtained by PE and paper recovery. Therefore, a specific recommendation was made to the managing consortium of the Industrial area of Prato to improve polymers collection (namely PE).

Luz et al. (2010) compared in a LCA context, the environmental impacts of sugarcane bagasse PP composites and talc PP composites used in the automotive industry. The FU of the study was the surface area covered inside one vehicle (m^2). The LCA was performed using the Gabi 4.3 software. The energy consumption of option 1 (sugarcane bagasse PP, 115 MJ) proved to be less than option 2 (Talc filled PP, 144 MJ) and the GWP for the treatment options tested (incineration, recycling and landfill) was calculated. Recycling proved to the most enviro-friendly option when compared with incineration.

Santoyo-Castelazo et al. (2011) used Gabi software to study the electricity generation in Mexico in a LCA context. The goal of the study was to estimate the life cycle environmental impacts of electricity generation from the public sector in Mexico, and the FU was defined as the total annual amount of electricity generated by the public sector. The main source of the GHGs was reported to be fossil fuelled operated plants, contributing 87% to the GWP. The AP was also assessed in the study and over 65% of 1.5 million tonnes of SO_2-eq per annum was estimated from the operation of heavy fuel oil power plants, mainly due to the high sulphur content (3-4%) of the oil used. The second largest contributor was the operation of coal power plants (20%).

A study carried out by the Milan Polytechnic Institute was reported by Rigamonti et al. (2009). The aim of this study was to determine the optimum level of separate collection in an integrated post consumer material system in Milan, Italy, and the environmental and energy impacts were assessed using the SimaPro 7 software and three integrated scenarios were modelled. The scenarios differed with each other in the quantity sent to material recovery and energy recovery. The main conclusions of the study can be summarised as follows:

- For all the analysed materials, recycling is more efficient when compared with incineration.
- The highest energy saving is related to aluminium recovery.
- Incineration with energy recovery is environmentally preferable when the electricity produced is replaced (off-set) with electricity produced from coal. However, incineration is less preferable when electricity is replaced with electricity produced from natural gas in combined cycle plants.

Eriksson et al. (2007) performed a CLCA with the aim of comparing district heating based on waste incineration with combustion of biomass or natural gas. The FU was 42 PJ (1 Petajoule = 1×10^9 MJ) of district heat, which is the amount released from incinerating all the waste in the study. Five technologies were compared with different fuel and/or energy recovery levels. These were: incineration with CHP production, incineration with district heat production only, biomass combustion with CHP production, biomass combustion with district heat production only, and natural gas combustion with CHP production. Avoided treatments were material recycling and landfilling. These avoided treatments were off-set against marginal data for wind, nuclear, biomass with CHP, coal, oil condense, hydro power and natural gas with CHP. Fourteen scenarios were developed by combining the different fuel types, energy recovery methods, avoided treatment and electricity scenario (based on marginal data), and the study was implemented using SimaPro 5 software. The main focus of the results was on the GWP impact assessment. Waste incineration with avoided landfilling scenarios gave the largest savings in GWP, regardless of the type of avoided electricity mix. Out of these, incineration with CHP gave the largest savings, especially for a high impact electricity mix. Biomass combustion performed the best with CHP, especially in combination with a replaced high gas price fossil intense power.

In this thesis, the Gabi 5 software was used to verify the calculations performed numerically using Microsoft Office EXCEL 2003 (see Chapter 6). The data level in Gabi 5 is considered very high, comprehensive and has proven to be a useful tool historically (Buttol et al., 2007; De Feo and Malvano, 2009; Tarantini et al., 2009; Rigamonti et al., 2009; Valerio, 2010). The database for the software enables the calculation of different impact categories (e.g. GWP

expressed in Kg $CO_{2\text{-eq}}$, AP expressed in $SO_{2\text{-eq}}$, etc), an advantage in using software packages in modelling scenarios. In contrast, a lack of specific details in the exact methodology of the compiled results is a disadvantage when using such commercial software. In addition, non-transparent datasets used by the software (e.g. transportation load calculations) pose a further disadvantage.

5.6. TCT Reactors, Incineration Processes and Recycling

Prior to the Environmental Act (1990), emissions in the UK were subject to single medium regulations covering releases to air, water and land. In 1976 the Royal Commission on Environmental Pollution highlighted that this was not an effective approach, and in 1999, the Integrated Pollution Prevention and Control EC Directive was implemented in the UK. Arena et al (2003a) conducted a LCA study focusing on the mechanical recycling option of PET and PE rigid packs within the Italian system. Six different scenarios, integrated by means of the combined use of the data gathered, were compared in terms of environmental burdens and resource consumption. The analytical comparison revealed that recycling was the best option when considering the hypothetical scenario of mechanically recycling all the collected waste. Although the case study did not reflect the reality of the situation, it emphasised how environmentally-friendly recycling can be, compared to energy recovery via incineration and landfilling. In a follow up study, Arena et al. (2003b) reported on the environmental burdens and materials consumption of the three different scenarios for the region of Campania, Italy. Landfilling was compared against RDF production and combustion and mass incineration, which proved to be a more viable strategic plan in terms of the environmental impact categories considered.

Khoo (2009) evaluated eight thermal technologies in Singapore, namely: pyrolysis of MSW, pyrolysis-gasification of MSW, gasification of MSW, pyrolysis-gasification-oxidation of MSW, steam gasification of wood, CFB gasification of organic waste, gasification of RDF and gasification of tyres. Environmental impacts were determined using LCA focusing on the GWP, AP, eutrophication and ozone photochemical formation. The study focused on the production of product gas from an assortment of waste types chosen for their importance as intermediates for the production of other industrial products, including methanol, ammonia, etc. Total life cycle costing was introduced and Equation 5.12 was used to calculate this for each system:

$$C_T = [C^P] \times [X_W] - [C^W] \times [X_W] + [C^L] \times [MSW_T / X_W \; residues] \qquad (5.12)$$

where C_T, C^P, C^W, C^L are the total processing, waste collection and landfilling costs, respectively. MSW_T is the total MSW generated (tonnes) and X_w is the amount of waste feedstock for generating 1 tonne of product gas. The highest cost was calculated for tyres

gasification, whilst the RDF gasification was determined to be the lowest. The pyrolysis-gasification of MSW option was determined to be the lowest in terms of AP, however the pyrolysis of MSW was determined to be the lowest in GWP (kg CO_2-eq). Vink et al. (2003) used LCA to compare polylactide (PLA), a versatile polymer used to replace a number of conventional conversion plastic product materials, against a number of petrochemical based ones. Nylon 66 was the highest in terms of fossil fuel requirements, and nylon 6 was the highest in kg CO_2-eq emission per kg polymer, when compared against polylactide (PLA), PCA, PS, PET and LDPE.

Finnveden et al. (2005) evaluated different strategies for the treatment of solid waste in Sweden based on a life cycle perspective. The main goal was to identify advantages and disadvantages of the different methods for the treatment of solid waste. The waste materials included were food waste, newsprint, corrugated cardboard, mixed cardboard, PE, PP, PS, PVC and PET. The treatment methods considered were incineration (of all fractions) with heat recovery, landfilling (of all fractions) with landfill gas extraction, recycling (of all fractions except food waste), AD (of food waste) and large scale composting (of food waste). The FU of the study was the amount of waste fractions collected in Sweden during one year and the scenarios considered in the study were all established from a base scenario, which had relatively shorter transport distances than the rest. The remaining scenarios considered were developed based on transport distance and method, time period of scenario or avoided energy treatment (heat from natural gas or forest paper recycling replacing natural gas). A number of conclusions were drawn from the study and these can be summarised as follows:

- Energy turnover for all treatment methods is negative for the whole system. This implies that the energy output from the system is larger than the energy input (excluding the energy content of the waste, which is constant in all cases and therefore disregarded).
- For PET, the emissions contributing to global warming from incineration were similar to the emissions from landfilling. This is because all the fossil carbon is released during incineration, as well as during landfilling.
- Recycling of paper and plastic materials is more favourable with regard to overall energy use, emissions of gases contributing to global warming and the total weighted results.
- In the system studied, heat from the incineration of waste replaced either heat from forest residues or natural gas. If the waste can replace oil or coal as energy sources, and neither biofuel nor natural gas is an alternative, then a policy promoting incineration may be successful for paper materials regarding emissions of GHGs.

The second part of the study was published with the aim of testing the validity of the waste management hierarchy for the treatment of solid waste (i.e. re-use being most favourable and landfilling being least, Moberg et al., 2005). This was accomplished via a LCA on recycling, incineration with heat recovery and landfilling of recyclable waste in Sweden, and the same scenarios previously described in Finnveden et al. (2005) were considered. The different waste management options studied were landfilling, incineration, recycling of paper and plastic fractions, and digestion and composting of food waste. The main conclusion presented in the study was that the waste hierarchy is valid as a rule of thumb. Another conclusion was withdrawn regarding the considered energy recovery aspect. Even though 50% of the landfill gas was assumed to be collected and combusted with energy recovery, this only makes up part of the potential resource that the waste may constitute if treated by recycling or incineration.

Björklund and Finnveden (2005) reviewed LCA studies of individual materials in household waste between the years 1995-2005. These materials included: PE, PET, aluminium, glass, cardboard, paper, newspapers, timber, naphtha, heavy oil, combustible gas, methanol and olefins, and publications focusing on recycling versus incineration and landfilling were reported. In terms of total energy and GWP categories, the reviewed studies were fairly consistent. Recycling showed the lowest impact on total energy use and GWP in most of the studies. Four key factors were identified from which it was possible to largely explain the few conflicting results: type of recycled materials, type of materials avoided by recycling, energy sources avoided by energy recovery from incineration, and the time perspective of landfills (i.e. a longer time perspective assumes that landfill decomposition will continue to cause environmental impact until all the material has been spread to the environment, and vice versa). Results from Denmark indicate that feedstock recycling is less favourable than the incineration of plastics with regard to GWP. However, this is contradicted by results from Germany, where feedstock recycling (TCT implementation) is the preferable option. Feedstock recycling produces high value output, but typically has high energy consumption, which reduces the overall performance (Björklund and Finnveden, 2005). Another notable point in the results presented was the fact that for plastics, landfilling can be preferable to incineration regarding GWP if the landfill is considered for a short time perspective. This is due to the 100 year time perspective of which there is no significant decomposition of plastic polymers and thus no GWP contribution. Economical analysis and overall costing were both lacking in the work presented. The profitability of a scenario often drives the implementation of the process, especially if scenarios have a similar environmental impact.

In conclusion, LCA, both attributional and consequential, has been implemented in a number of studies to determine the best performance of processes, engineering solutions, waste management scenarios and disposal methods (Nicholas et al., 2000; Arena et al., 2003a, 2003b,

Perugini et al., 2005; Moberg et al., 2005; Finnveden et al., 2005). LCA accounts for every stage in the cycle of the product or service, from resource extraction (cradle) to the ultimate end-of-life treatment (grave), and hence the term 'life cycle' is employed.

The LCA structure consists of four very distinct phases that contribute to an integrated approach to waste management. These phases are (in consequential order): (i) goal and scope definition; (ii) LCI or inventory analysis; (iii) LCIA or impact assessment, and finally; (iv) interpretation. Previous LCA reports have confirmed that recycling uses less energy than classical methods of waste disposal, i.e. landfilling (Buttol et al., 2007). Recycling also emits the lowest volatile organic compounds when compared to incineration and landfilling (Buttol et al., 2007). Improving the recovery of polymers (namely PE) has been reported to reduce environmental indicators (Tarantini et al., 2009).

Incineration with energy recovery in CHP plants are environmentally preferable when the electricity produced is off-set against electricity produced from coal (Rigamonti et al., 2009). According to Eriksson et al. (2007), incineration in a CHP process gives the largest savings, especially for a high impact marginal electricity mix. However, Valerio (2009) recommends referring to the average electricity mix when off-setting electricity production. Past reports taking into account the production of national electricity mix to evaluate avoided electricity generation (i.e. off-setting against the national grid) (Valerio 2009, Rigamonti et al., 2009), confirm that recycling is the best option for energy savings and toxic environmental impacts in many geographical contexts (Europe, USA and China).

Björklund and Finnveden (2005) confirmed that recycling showed the lowest impact on total energy use and GWP in most of the studies reviewed. Regarding TCT of plastics (especially feedstock recycling), results from Germany show such processes as the preferable option in terms of GWP against incarnation. Feedstock recycling produces high value output, but typically also has a high energy consumption, which reduces the overall performance (Björklund and Finnveden, 2005). Another notable point in the results presented was the fact that for plastics, landfilling can be preferable to incineration regarding GWP if the landfill is considered within a short time perspective. This is because there is no significant decomposition of plastic polymers within a 100 year time perspective and thus no GWP contribution.

As a method for systematic environmental assessment, LCA still lacks clarity, sophistication and the proper complexity in its LCIA. A lack of complexity is the direct result of data availability in the literature and published reports. Clear calculations regarding reported impacts are also very scant, and typically one must rely on weighting methods. Furthermore, authors neglect the clear detailing of avoided burdens and in addition, the distinction between types of LCA (i.e. consequential and attributional) is rarely made clear.

This thesis undertakes a LCA study set in the GLA, which includes waste inputs and outputs, energy assessments and economic analyses of MRFs, TSs and other unit operations (see Chapter 6). In addition, implementing TCT units and their impact on existing systems has not been attempted previously for the City of London. The gaps in the recent research are addressed by the work presented in this thesis (see Chapter 6). The study carried out focuses on identifying and quantifying the environmental burdens, namely GWP and energy turnover associated with the life cycle of polymers treatment in the GLA. Three scenarios are defined to include conventional routes of treatment in London (dry product recovery through a MRF and incineration with CHP production), as well as implementing two TCT industrial units (pyrolysis and hydrogenation reactors) to the baseline scenario. Avoided treatments, such as landfilling, UK average grid mix and marginal electricity production, etc., where also included in developing the overall system studied. Landfilling was also compared to the system studied to demonstrate the effects of treating the FU in the studied scenarios with the unit operations investigated in this study. This type of analysis is classified as an ALCA, where average data are used to reflect the burdens quantified for all unit operations involved.

Chapter 6

Life Cycle Assessment of Utilising Polymeric Fractions of MSW in the Greater London Area

The aim of this chapter is to present the results of an attributional life cycle assessment (ALCA) study performed for three integrated scenarios reflecting the management, treatment and handling of polymers in the context of municipal solid waste (MSW) in the Grater London area (GLA). The study comprises a materials recovery route via a dry materials recovery facility (MRF), an energy recovery route (incineration unit (IU) with combined heat and power) and two thermo-chemical treatment (TCT) units with industrial scale technologies. The TCT units consist of a low temperature pyrolysis (LTP) reactor working under BP® technology and a Veba-Combi Cracking (VCC®) hydrogenation reactor. The LTP process recovers petrochemicals (e.g. gases (C_3-C_4), liquid fractions (naphtha), waxes (atmospheric residue, AR) and heat in the form of steam, whilst the VCC® process produces syncrude and e-gas which is comparable to natural gas. All the petrochemicals, chemicals, CO_2 emissions and energy produced by the different technologies were considered as a credit to the overall system developed, due to the fact that the treated functional unit (FU) is of MSW origin and the technologies are all EfW processes.

The system expansion methodology was applied to the three integrated scenarios (see Section 5.3.1). The following alternatives were off-set: average electricity (UK mix) production, four alternatives for marginal electricity generation (natural gas, wind, hard coal and nuclear) and the UK combined cycle gas turbine (CCGT) heat generation marginal data for off-setting heat production from IU with CHP) (see Section 5.3.1). All the scenarios developed were compared to landfilling the amount entering the overall system (i.e. the FU). The study investigates the

impact of introducing TCT units with the aim of petrochemicals recovery on the environment. All the calculations reported in Section 6.3 were undertaken using Microsoft Office Excel 2003, and the results obtained were later validated using Gabi 5 software.

Parts of this chapter were published in:

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2008**). Waste to energy solutions from polymeric based solid waste in the context of Life Cycle Assessment (LCA), In: Proc 2nd Energy Materials at UCL-Centre for Material Research Forum Meeting, pp. 19. London (*England*), UK, 3rd December.

Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**). Petrochemicals recovery through polyethylene (PE) pyrolysis: Maximizing product yields via isothermal and dynamic kinetics, In: Proc Energy from Biomass and Waste UK (EBW UK) Conference and Exhibition, London (*England*), UK, 26th-27th January.

Al-Salem, S.M., Mechleri, E., Papageorgiou, L.G. and Lettieri, P. (**2012**). Life cycle assessment and optimization on the production of petrochemicals and energy from polymers for the Greater London Area, *Computer Aided Chemical Engineering,* **30(1)**, 101-106.
Also in: Proc of the 22nd European Symposium on Computer Aided Process Engineering (ESCAPE 22), Part A; Edited by: Bogle, D., Fairweather, M., pp. 101-106, Elsevier. London (*England*), UK, 17th-20th June.

6.1. Background, Problem Statement and Objectives: What Happens to Plastics in the Context of MSW Produced in the Capital?

Municipal solid waste (MSW) is by far the most heterogeneous of all refuse (Pellencst, 2010), and is the result of activities in the urban environment (cities, villages, municipalities). MSW consists of an organic fraction (wet waste: kitchen waste, food waste, straw, garden trimmings, sawdust, etc.) and a non-organic fraction (dry waste: glass, plastics, metals, ash, atone and bricks, etc.). The properties of waste differ immensely depending on many factors, such as the area of collection (rural, urban, industrial or commercial), seasonal variations and recycling levels (Yassin, 2007). For example, the fraction of plastics in MSW assessments differs significantly between countries; in the USA, plastics represent 12.1% of MSW (USEPA, 2008), whereas in the state of Kuwait (a Middle Eastern country depending heavily on crude oil production), it represents 13% of the final stream of MSW (Al-Meshan et al., 2001). According to the UK Waste and Resources Action Programme (WRAP), PSW amounts to 7% of the UK MSW final stream and the UK consumes over 5 million tonnes of plastics annually. In this study, the waste fractions breakdown used in the technical and economic assessment are the

official Governmental assessment of MSW in the UK published by Parfitt (2002) for the UK WRAP. Figure 6.1 reports the waste percentages considered in this study.

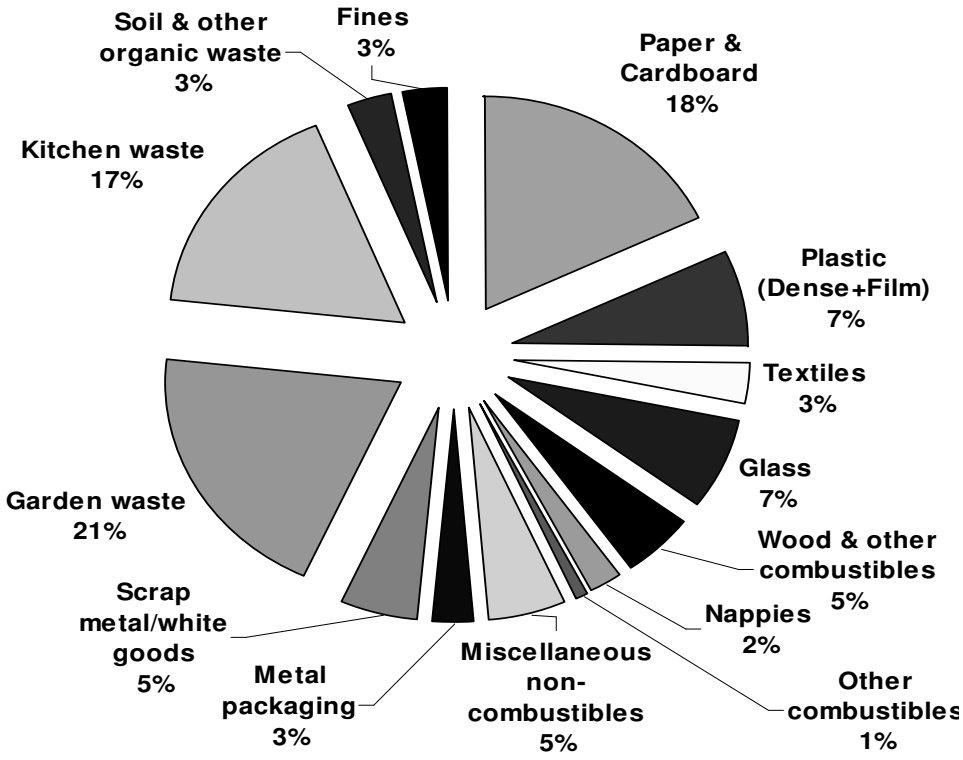

Figure 6.1 - Waste breakdown in the UK used in this study. Source: Parfitt (2002).

Plastic solid waste (PSW) produced in the UK capital is typically collected by different councils, boroughs, waste authorities and contractors. PSW ends up in different transfer stations (TSs) (see Section 2.2.1.) which distribute the waste to the relevant processing lines (Last, 2008a; 2008b). Waste management activities in and around London include waste incineration and materials recovery.[1] Furthermore, the current economic climate gives PSW a new perspective as a sustainable feedstock. Since polymers have a high calorific value (see Table 2.1), treating PSW thermo-chemically is a more preferable route to dry recovery processes (i.e. recovery through MRFs alone), incineration processes and the conventional route of landfilling. Since thermo-chemical treatment (TCT) processes recover a number of valuable petrochemicals (e.g. gases (C_3-C_4), liquid fractions (naphtha), waxes (AR), syncrude, e-gas and energy (typically in the form of heat), utilising PSW as a feedstock for such processes on an industrial scale warrants investigation and further study. This chapter reports the results of a life cycle assessment (LCA) study conducted on a system developed that comprises of a materials recovery route via a dry materials recovery facility (MRF), an energy recovery route (CHP IU) and two TCT industrial scale technologies. The TCT units are a LTP reactor working under BP® technology and a VCC® hydrogenation reactor.

[1] Personal Communication: Mr. Terry Dickinson (Greenwich MRF Site Manager, Dec 2009).

Available reports in the literature are typically council reports or private consultancy findings (Didsbury, 2006; Waste Watch, 2003; ADAS, 2008). The UK Office for National Statistics (ONS, 2009) published in their 2009 report the amount of co-mingled waste produced by each individual in the country (0.495 tpa of total waste per resident). This value was considered in this study in order to determine the total amount of waste produced in each borough served by the MRF station and the CHP IU plant (see Sections 6.2.1-6.2.2). Table 6.1 indicates the population of each borough and the breakdown of waste fractions considered in this study. The plastics breakdown (%) is shown in Table 6.2.

The Greenwich MRF (see Section 6.2.1) processes the dry fraction generated from the Boroughs of Greenwich and Lewisham, as well as the City of Exeter, Devon. This amounts to 137,303 tpa, which was considered to be the MRF throughput in this analysis. The IU (see Section 6.2.2) processes co-mingled waste generated from the Boroughs of Greenwich, Lewisham, Westminster and Bromley. In addition, the IU feed stream also includes 30,000 tpa of collected waste from the GLA (SELCHP, 2010). In this study, the latter was assumed to be organic waste as no details on the waste composition were available. Furthermore, no glass or metals were assumed to enter the IU feed stream and hence the glass, metals packaging and white goods fractions generated from Bromley and Westminster (39,468 tpa) were excluded from the IU throughput. This assumption was made due to the fact that the MRF receives dry waste from three points of origin only (Greenwich, Lewisham and Exeter). The excluded waste fractions consisting of metals and glass amounts to 39,468 tpa; therefore, the IU throughput feed consists of the wet waste fractions generated by Greenwich, Lewisham, Bromley and Westminster. It also includes the 30,000 tpa of organics collected from the GLA and it was also assumed that the wet fraction of Exeter is sent to the IU plant. This is consistent with the maximum capacity of the IU plant (420,000 tpa) declared by the company (SELCHP, 2010). This also services the integration strategy undertaken in this work, by delivering the waste from similar points of origin to the unit operation lines. Therefore, the IU throughput amounts to 414,838 tpa, which is equal to the total amount of organics from all the boroughs (303,269 tpa), total amount of plastics (18,418 tpa), fines (7,894 tpa), textiles (7,894 tpa), paper and cardboard (47,362 tpa) from Westminster and Bromley and 30,000 tpa of collected organic waste from the GLA.

Table 6.1 Boroughs considered in the study showing the waste breakdown and location of recycling centre chosen.

Borough	Greenwich (B1)	Lewisham (B2)	Exeter (B3)	Westminster (B4)	Bromley (B5)
Population	222600	261600	118800	236031	295532
Waste generation (tonnes/year)*	110187	129492	58806	116835	146288
Plastic (dense + film) (tonnes/year)	7713	9064	4116	8178	10240
Textiles (tonnes/year)	3306	3885	1764	3505	4389
Glass (tonnes/year)	7713	9064	4116	8178	10240
Metal packaging (tonnes/year)	3306	3885	1764	3505	4389
White goods/metal (tonnes/year)	5509	6475	2940	5842	7314
Fines (tonnes/year)	3306	3885	1764	3505	4389
Paper & cardboard (tonnes/year)	19834	23309	10585	21030	26332
Dry Fraction (non-organic) (tonnes/year)**	50686	59566	27051	53744	67293
Organic waste (tonnes/year)***	59501	69926	31755	63091	78996
Recycling centre chosen	Birchmere Depot	Re-use & RC	Devon RC	Cringle Dock TS	Civic Centre

* Considering 0.495 tonnes of waste generated/resident. *Source*: ONS (2009).
** Dry fraction of waste was considered as 46% of the total waste, which includes the following: Plastics, textiles, glass, metal packaging, white goods/metal, fines, paper and board.
*** Organic waste was considered as the remaining fraction, which amount to 54%.

Table 6.2 Polymer by Type in Each Borough.

Borough	Percentage*	Greenwich (B1)	Lewisham (B2)	Exeter (B3)	Westminster (B4)	Bromley (B5)
Plastic amount (tonnes/year)	-	7713	9064	4116	8178	10240
Polyethylene (LDPE+HDPE)	37.5 (24.3+13.2)	2892	3399	1544	3067	3840
Polypropylene (PP)	18.5	1427	1677	762	1513	1894
Polyvinyl Chloride (PVC)	18.8	1450	1704	774	1538	1925
Polystyrene (PS)	6.3	486	571	259	515	645
Rest	18.9	1458	1713	778	1546	1935

* *Source*: Waste watch (2003).

The work presented in this chapter attempts to answer the following questions by conducting an ALCA on three different integrated scenarios that reflect the management of MSW in London:

- By implementing industrial scale thermo-chemical treatment (TCT) units, will the overall system developed be more environmentally friendly?
- Can the thermo-chemical treatment (TCT) units implemented improve the system developed financially by increasing its techno-economic performance?

The specific methodological aspects are described in detail below. Mass and energy calculations with respect to each process and activity are shown, and in addition, the analysis takes into account the products and energy displaced. The amount of energy or product is subtracted by the amount resulting from an alternative method (i.e. off-setting); thus, avoided emissions will occur and environmental interventions may be negative. In such reports, the system is said to be credited with an equivalent amount of product (e.g. heat, electricity, etc.) being produced in an alternative manner. This procedure is in line with the system expansion methodology (see Chapter 5) which enables different waste management systems to be compared and can be used to evaluate product/material displacement.

6.2 Developing the Integrated Scenarios

In order to develop an overall system that reflects the current waste management in London, the conventional treatment practices for waste management must be considered. In London, waste is mainly treated by material recovery (through dry MRFs) or by incineration units (IU, operating in a CHP process).[1] Consequently in this work, a MRF was chosen to operate alongside an IU to produce heat and power. The MRF chosen is an actual dry facility located in Greenwich. In addition, the IU is an actual plant located in Lewisham that operates a mass-burn industrial unit (South East London Combined Heat and Power, SELCHP). Details of each will be illustrated in the following sections. In reality, both plants operate on a standalone basis, i.e. with no exchange of material between their waste treatment activities. However, in this study the overall system developed, based on integrating the operations of these two plants and the source of feed to provide a more efficient and environmentally friendly solution will be investigated. The functional unit (FU) of this study was considered to be 552,141 tpa, which is equal to the combined total of the MRF and the IU throughput.

The study also includes the environmental impacts expressed as global warming potential (GWP) and calculated as kg $CO_{2\text{-eq}}$. The avoided burdens in the IU were also considered by

[1] Personal Communication with Mr. Terry Dickinson (Greenwich MRF Site Manager, Dec 2009).

displacing electricity and heat production, whilst the products of the MRF station are also displaced by their commercial production process. The incineration bottom ash (IBA) recovered is off-set against commercial aggregate production and the products of the TCT industrial units are also displaced by commercial refining and petrochemicals processes. Figure 6.2 shows the overall system investigated in this work, indicating the foreground system (resulting in direct burdens), background system (resulting in indirect burdens) and the avoided burdens displaced. The background system includes a compensatory supply system for the power input and other auxiliary processes (electrical inputs to unit operations, etc.).

The total life cycle inventory in this study was reported as the sum of the following (Clift et al., 2000):

Direct burdens (resulting from the Foreground)	+	Indirect burdens (resulting from the Background)	-	Avoided burdens (resulting from the displaced products)

In this study, three integrated scenarios for the processing of MSW are considered. Scenario 1 (baseline) considers the conventional route of waste treatment (MRF+IU), whilst scenarios 2 and 3 incorporate a pyrolysis and a hydrogenation reactor, respectively. The different combinations of the scenarios investigated are summarised in Table 6.3 and each scenario is schematically represented in Figures 6.3-6.5. The electrical production was displaced using average and marginal data (i.e. UK electricity mix, nuclear, hard coal, wind and natural gas). The combinations studied were also compared to a landfilling scenario (combination 1) in which all the waste is directly sent to landfill.

In the UK, the proximity principle has been described and implemented in many facilities involving energy from waste (EfW) treatment, and it has been part of the IU (SELCHP) operation described in Section 6.2.2, and other EfW schemes (Yassin, 2007; SELCHP, 2010; DECC, 2010). The principle is concerned with treating the waste as close as possible to its point of origin and in this study, the proximity principle was considered in the development of the overall system studied. The TCT units are all assumed to be on the same location as the MRF station to avoid the extra travelling distance to deliver the plastic feed to the LTP or hydrogenation unit. By developing the overall system thus, the proximity principle is met.

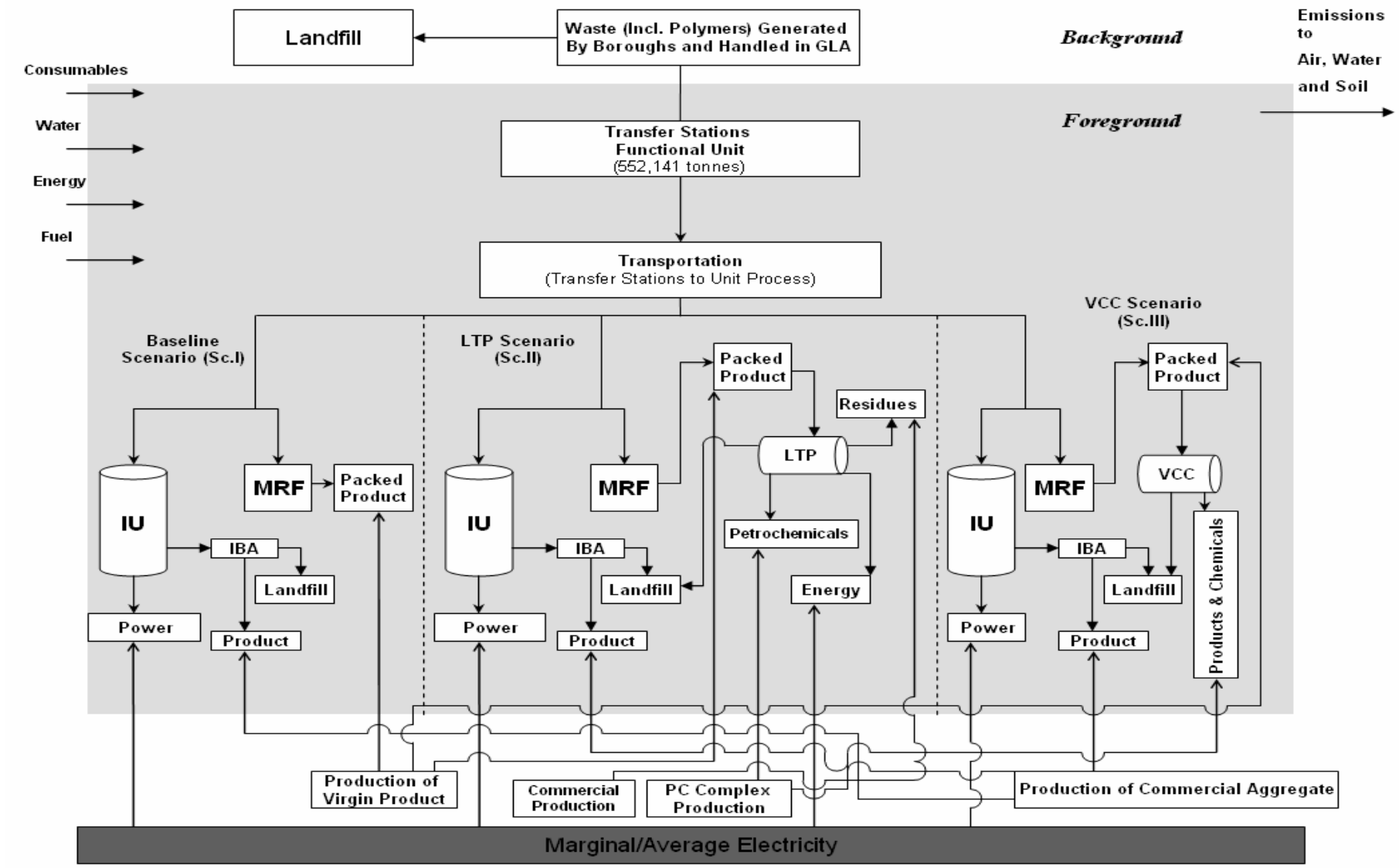

Figure 6.2 - Overall LCA Scenarios Investigated.

Table 6.3 Combinations Studied in this Work.

No.	Energy Recovery Method	Scenario Considered	Electricity Production Technology	Heat Production Technology	Avoided Burden (Off-set)
1	Landfill EfW	Landfilling the FU	-	-	EfW EU25 Model
2	CHP IU	Scenario 1	UK Grid Mix	UK CCGT	MRF Products, landfill, IBA and power
3	CHP IU	Scenario 1	UK Marginal Natural Gas	UK CCGT	MRF Products, landfill, IBA and power
4	CHP IU	Scenario 1	UK Marginal Nuclear	UK CCGT	MRF Products, landfill, IBA and power
5	CHP IU	Scenario 1	UK Marginal Hard Coal	UK CCGT	MRF Products, landfill, IBA and power
6	CHP IU	Scenario 1	UK Marginal Wind	UK CCGT	MRF Products, landfill, IBA and power
7	CHP IU and Heat from LTP	Scenario 2	UK Grid Mix	UK CCGT	MRF Products, landfill, IBA and power
8	CHP IU and Heat from LTP	Scenario 2	UK Marginal Natural Gas	UK CCGT	MRF Products, landfill, IBA and power &LTP products
9	CHP IU and Heat from LTP	Scenario 2	UK Marginal Nuclear	UK CCGT	MRF Products, landfill, IBA and power &LTP products
10	CHP IU and Heat from LTP	Scenario 2	UK Marginal Hard Coal	UK CCGT	MRF Products, landfill, IBA and power &LTP products
11	CHP IU and Heat from LTP	Scenario 2	UK Marginal Wind	UK CCGT	MRF Products, landfill, IBA and power &LTP products
12	CHP IU	Scenario 3	UK Grid Mix	UK CCGT	MRF Products, landfill, IBA and power &VCC products
13	CHP IU	Scenario 3	UK Marginal Natural Gas	UK CCGT	MRF Products, landfill, IBA and power &VCC products
14	CHP IU	Scenario 3	UK Marginal Nuclear	UK CCGT	MRF Products, landfill, IBA and power &VCC products
15	CHP IU	Scenario 3	UK Marginal Hard Coal	UK CCGT	MRF Products, landfill, IBA and power &VCC products
16	CHP IU	Scenario 3	UK Marginal Wind	UK CCGT	MRF Products, landfill, IBA and power &VCC products

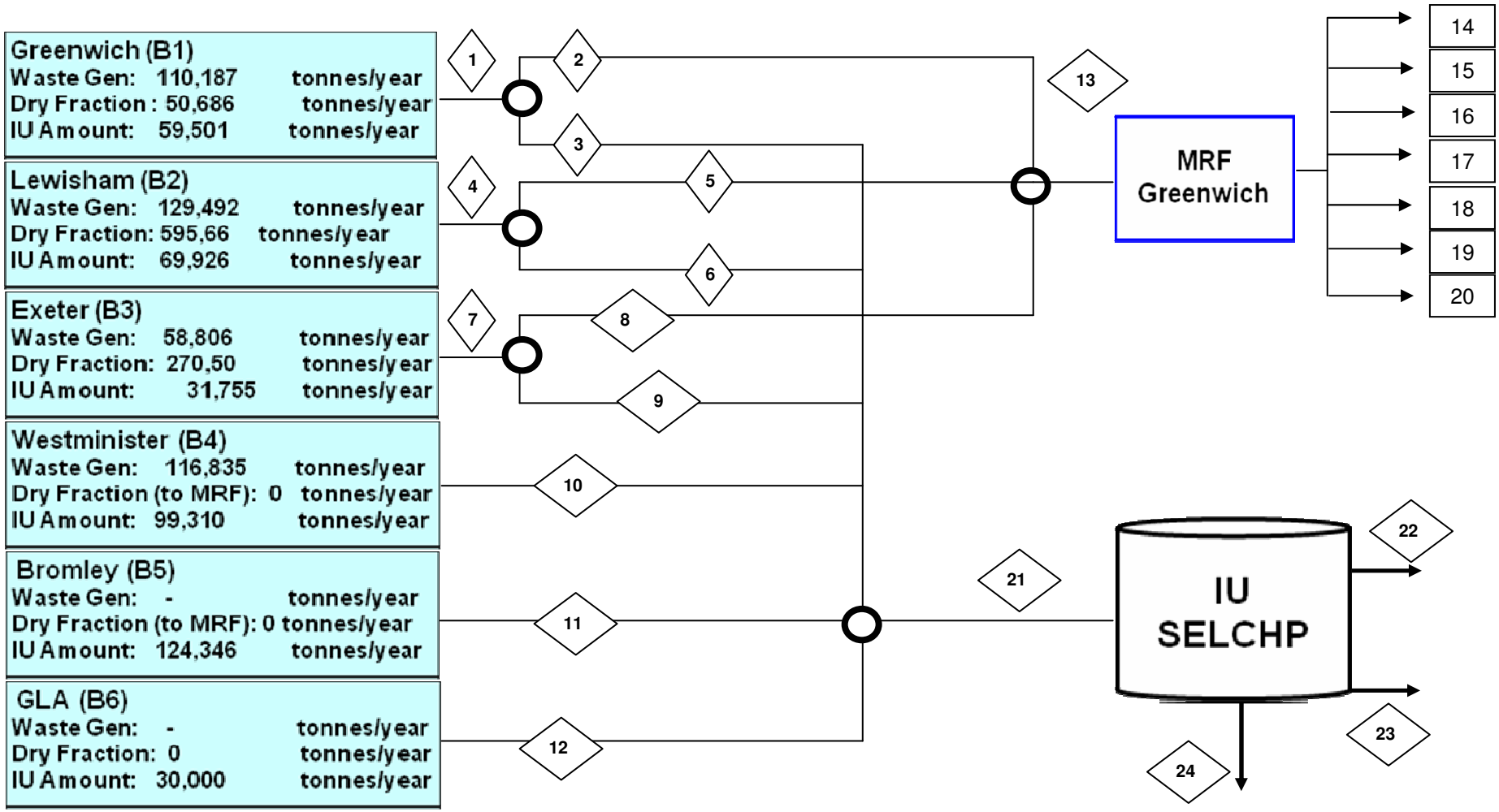

Figure 6.3 - Scenario 1 Flow Diagram.

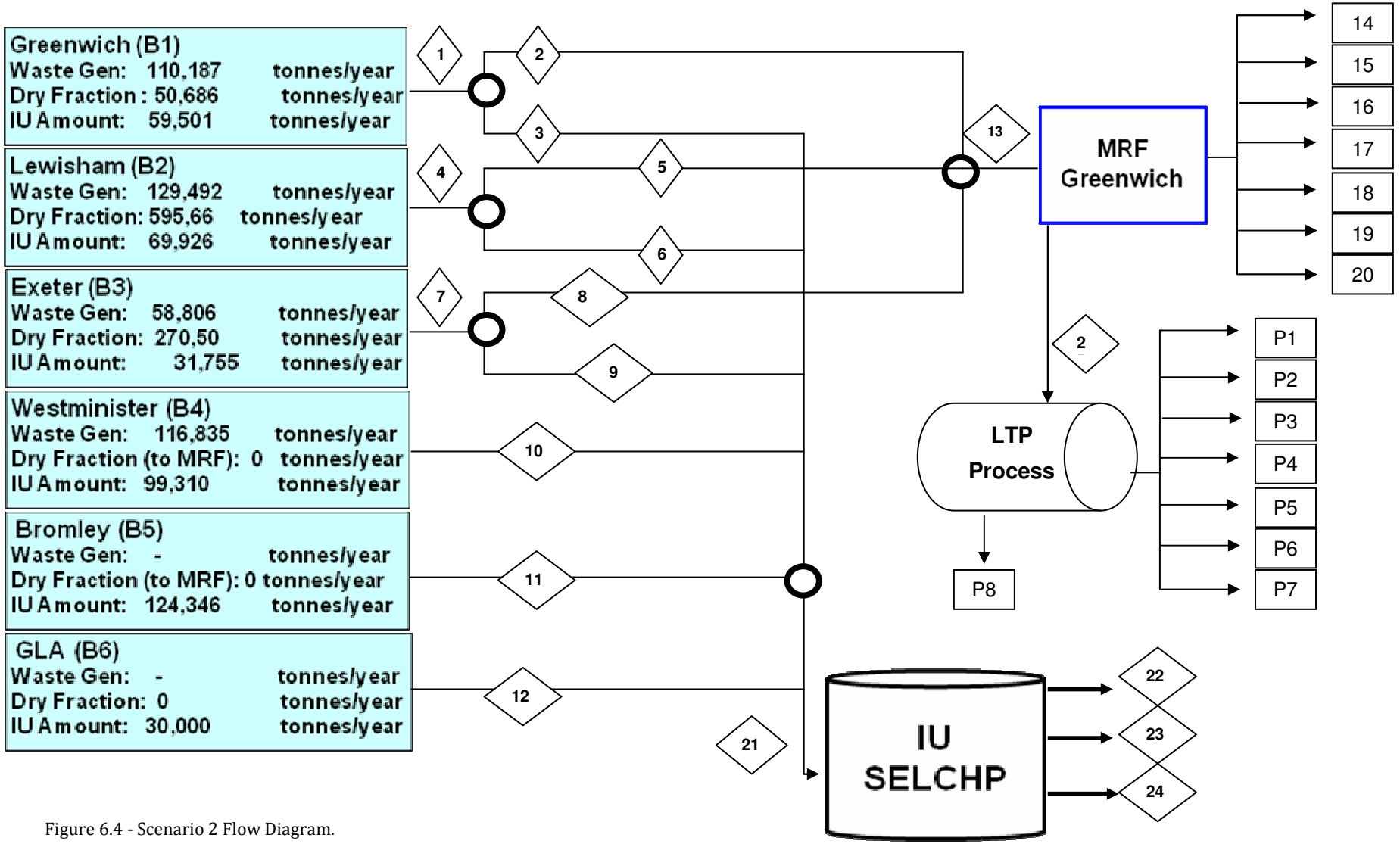

Figure 6.4 - Scenario 2 Flow Diagram.

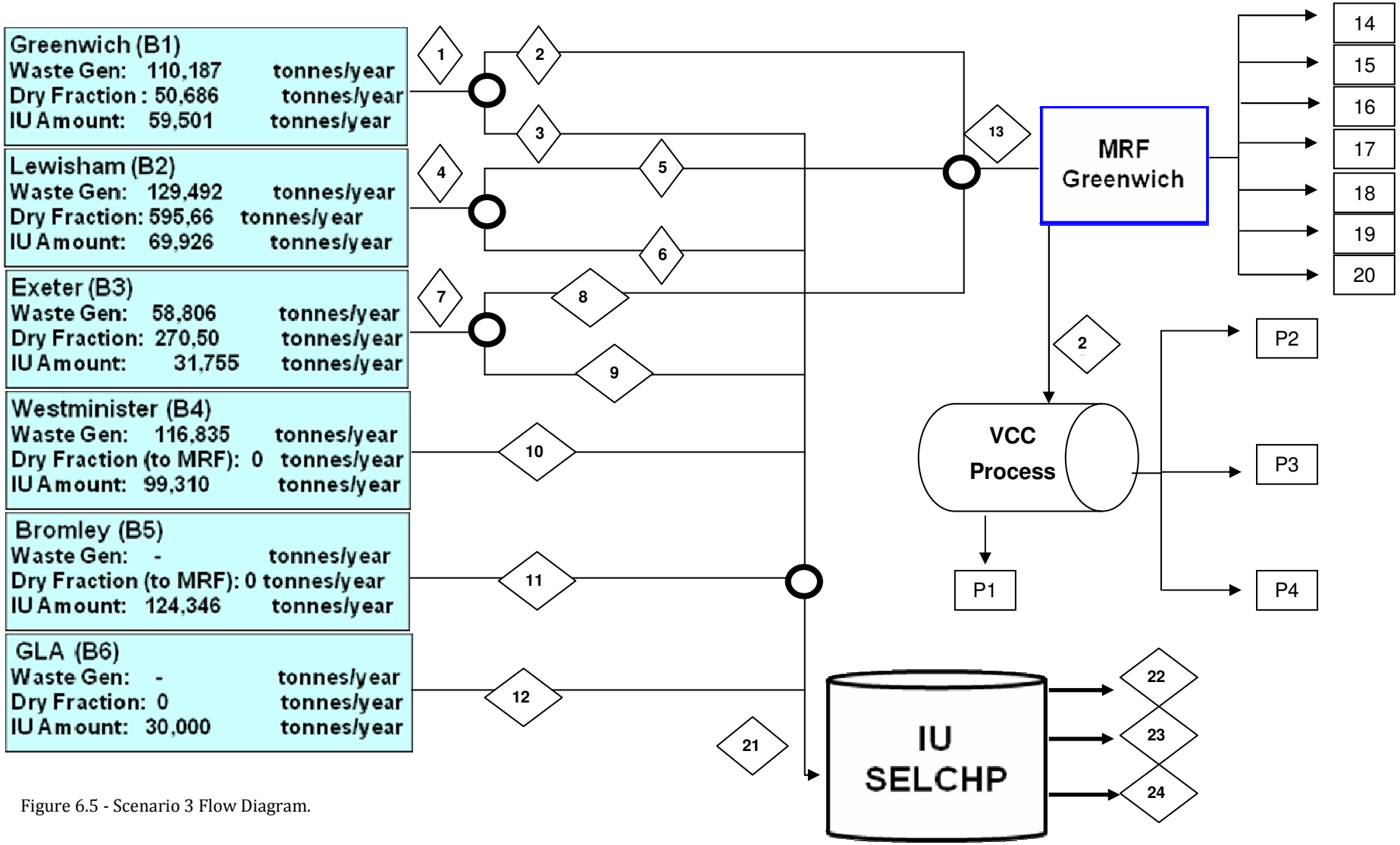

Figure 6.5 - Scenario 3 Flow Diagram.

Table 6.4 Key to Scenario 1 Flow Diagram

No.	Flow Quantity	Unit	Notes	No.	Flow Quantity	Unit	Notes
1	110,187	tpa		13	137,303	tpa	MRF Feed
2	50,686	tpa	Transferred to MRF	14	9,611	tpa	Plastics Recovered
3	59,501	tpa		15	4,119	tpa	
4	129,492	tpa		16	9,611	tpa	
5	59,566	tpa	Transferred to MRF	17	4,119	tpa	
6	69,926	tpa		18	6,865	tpa	
7	58,806	tpa		19	4,119	tpa	
8	58,806	tpa	Transferred to MRF	20	24,715	tpa	
9	99,310	tpa		21	414,383	tpa	IU throughput
10	99,310	tpa		22	3.82×10^8	kWh/year electricity	Electrical Generation
11	124,346	tpa		23	1.2×10^9	kWh/year heat	Heat Generation
12	30,000	tpa		24	82,968	tpa	IBA Produced

Table 6.5 Key to Scenario 2 Flow Diagram

No.	Flow Quantity	Unit	Notes	No.	Flow Quantity	Unit	Notes
1	110,187	tpa		17	4,119	tpa	
2	50,686	tpa	Transferred to MRF	18	6,865	tpa	
3	59,501	tpa		19	4,119	tpa	
4	129,492	tpa		20	24,715	tpa	
5	59,566	tpa	Transferred to MRF	21	414,383	tpa	IU throughput
6	69,926	tpa		22	3.82×10^8	kWh/year electricity	Electrical Generation
7	58,806	tpa		23	1.2×10^9	kWh/year heat	Heat Generation
8	58,806	tpa	Transferred to MRF	24	82,968	tpa	IBA Produced
9	99,310	tpa		P1	1470	tpa	Gas Fraction
10	99,310	tpa		P2	4480	tpa	Waxes
11	124,346	tpa		P3	2650	tpa	liquids
12	30,000	tpa		P4	400	tpa	CaO
13	137,303	tpa	MRF Feed	P5	770	tpa	$CaCl_2$
14	8,611	tpa	Plastics Recovered	P6	760	tpa	Sand
15	4,119	tpa		P7	460	tpa	Waxy Filter
16	9,611	tpa		P8	14800	MJ/year	P-Steam

Table 6.6 Key to Scenario 3 Flow Diagram

No.	Flow Quantity	Unit	Notes	No.	Flow Quantity	Unit	Notes
1	110,187	tpa		15	4,119	tpa	
2	50,686	tpa	Transferred to MRF	16	9,611	tpa	
3	59,501	tpa		17	4,119	tpa	
4	129,492	tpa		18	6,865	tpa	
5	59,566	tpa	Transferred to MRF	19	4,119	tpa	
6	69,926	tpa		20	24,715	tpa	
7	58,806	tpa		21	414,383	tpa	IU throughput
8	58,806	tpa	Transferred to MRF	22	3.82×10^8	kWh/year electricity	Electrical Generation
9	99,310	tpa		23	1.2×10^9	kWh/year heat	Heat Generation
10	99,310	tpa		24	82,968	tpa	IBA Produced
11	124,346	tpa		P1	822	tpa	Syncrude
12	30,000	tpa		P2	90	tpa	E-Gas
13	137,303	tpa	MRF Feed	P3	50	tpa	Solid Residues
14	8,611	tpa	Plastics Recovered	P4	4	tpa	CaC_{l2}

6.2.1. The Greenwich Material Recovery Facility Station

The increase in co-mingled waste has led to an increase in the number of MRFs in the UK, especially in England where there are currently 61 MRFs operating. The development of more MRF stations in the UK Capital was announced by the Mayor of London in 2008 (LALD, 2008). Currently, there are four MRFs operating in London:

1. Greenwich MRF - operated by Veolia Co.
2. Crayford MRF - operated by Grosvenor.
3. East London Waste Authority MRF (recently commissioned).
4. Western Riverside Waste Authority (recently commissioned).

A typical MRF will employ a system of conveyers to carry the waste over sorting screens, including inclined tables, air classifiers, etc. The carried waste will later be divided using magnetic and eddy current separators which may employ advanced optical recognition equipment (Last, 2008b).

The MRF station in Greenwich was visited in order to gather a more coherent insight on the current dry processing scheme being undertaken in the capital. The main purpose of the visit was to gather as much on-site data as possible in order to understand the operations involved with waste handling, especially plastics. The Greenwich MRF station operates within a closed loop system.[1] and is a dry-MRF type, i.e. no organics are present or treated in the processing line. The station accepts dry recyclables from the following:[2]

1. Borough of Greenwich (London).
2. Borough of Lewisham (London).
3. City of Exeter (Devon).

The Greenwich MRF station was considered in this study as the route for dry recyclables in the overall system developed and the maximum capacity of the station (146,000 tpa) was used in this study. The plant processing stages involve nine different separation steps that consume diesel and electricity, but no crude oil or steam is involved in the different processing stages of the plant. The first stage is the 'separation by size', whereby the fibres and containers are separated by a Trommel Machine which is fitted with a crash spoiler to crush: a) fibres (including paper, newspaper); and b) containers (plastic bottles, cans, containers). The second

[1] The closed loop system operated in Greenwich MRF involves the transport of waste from points of origin (Transfer Stations, boroughs, collection depots) to the plant, treatment of waste on-site and selling the recovered bulk with no waste fraction sent to landfill.

[2] Personal Communication with Mrs. Barbara Luvsby (2011) and Mr. Terry Dickinson (2009 Site Manager).

stage is the 'separation by type' step (or ballistic step), where an angle deck with peddles is used and the separation of 2D and 3D objects takes place (i.e. fibres and containers, respectively). The third stage is the 'rotating magnet' stage, where the main function is to separate steel from the main stream of waste; separated steel goes straight to storage bunkers. The fourth stage is the aluminium separation which is achieved via an 'electrical current'. Stage five is the 'disc screen', where glass is broken and paper is transferred to a separate machine. The sixth stage in the station is the 'manual sorting' where employees take all of the dry waste present that has escaped from the previous steps except for the paper. The seventh stage is the 'plastic sorting' step, which is typically undertaken according to market demands and sales figures and at the time of the visit, the market was demanding mixed plastic. Until 2011, sorting occurred for PET only, although the plant includes an option for sorting 'by laser' for four polymer categories: PET, HDPE, clear and coloured plastic. Stage eight is concerned with paper and newspaper sorting (transfer to storage bunkers). Lastly, the two 'hydraulic presses' are used to press the paper into cubic bulks ready for shipment and transfer. Figure 6.6 shows schematically the dry waste through the different stages of the MRF.

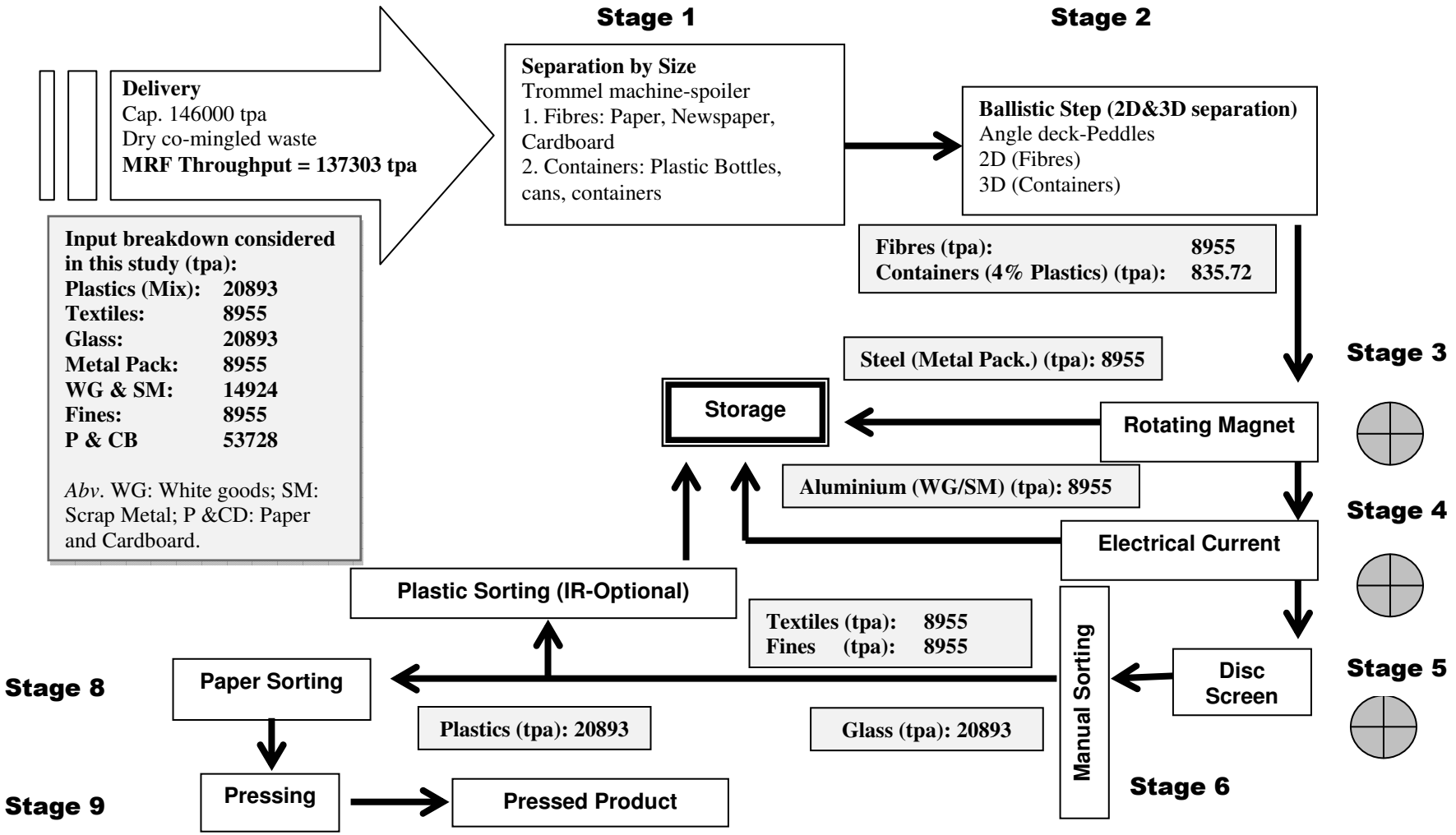

Figure 6.6 - Greenwich MRF Throughput Breakdown Considered in this Analysis. The ONS (2009) amount of waste generated by each individual in the UK, which is 0.495 tpa, was considered. The waste fractions breakdown of Parfitt (2002) was considered in this schematic and in this analysis in general.

Performing the energy and mass balances on the MRF represented in Figure 6.6 enables the comparison of the technical performances of the different treatment options and the scenarios considered in this study. The MRF station production line depends on the amount of dry waste fed into its processing line. The MRF consumes diesel in its different processing stages and diesel consumption was calculated with respect to the total MRF throughput, as shown in Equation 6.1 (ADAS, 2008).

$$\text{DC (litres)} = 1.73 \times \text{TP} \tag{6.1}$$

where DC is the total diesel consumed (litres) in the MRF station and TP is total co-mingled throughput of the MRF station (tpa). Equation 6.2 estimates the electrical consumption of the MRF station, as described by ADAS (2008).

$$\text{EC (kWh)} = 30 \times \text{TP} \tag{6.2}$$

where EC is the total electricity consumed in the MRF station (kWh) and TP is total co-mingled throughput of the MRF station (tpa). In this thesis, it was assumed that the MRF sends no waste fraction to landfill as this reflects the practice of the actual MRF station in Greenwich. In order to calculate the carbon emission (kg CO_2/year) resulting from the MRF processing line, the conversion factor of 2.68 kg CO_2/litre was used for the total amount of diesel consumption (UE, 2010).

Energy consumption contributes to the total carbon footprint of any establishment. The electricity mix in the UK consists of a number of contributing sectors that result in what is known as the average mix. These sectors and their contribution are as follows: natural gas (45%), hard coal (32%), nuclear (13.5%), hydro energy (2.4%), wind (2%), fuel oil (1.6%), biogas (1.4%), EfW (0.74%), biomass (0.7%) and coal gases (0.35%) (Gabi 5 DB V5.43). This electricity mix was used in this analysis to calculate the CO_2 emitted from the electricity consumed in the MRF, and the conversion factor of 0.05 kg CO_2/kWh was used to calculate the emitted carbon dioxide for the electricity consumed in the MRF station (Gabi 5 DB V5.43). The MRF station recovers dry recyclables that can be sold, including plastics, glass, steel, etc. In this work, the MRF credits the system developed by displacing the amount of CO_2 that would be produced by the conventional production methods. It was assumed that each product produced by the MRF replaces the conventional market product with a 1:1 ratio. The products separated in the MRF station were credited using the conversion factors reported in Table 6.7.

Table 6.7 Conversion Factors used to Credit the Overall System for the MRF Products against Commercial Virgin Products.

MRF Product	Commercial Product	kg CO_2-$_{eq}$/tonne Product	Reference
Plastics	Virgin LLDPE Production	2	Greene, 2012
Glass	Commercial Glass	8.4	GRB, 2012
Metal Packaging	Steel	1.1 (kg CO_2-$_{eq}$/kg Product)	TATA Steel, 2012
White Goods and Metal Scrap	Steel	1.1 (kg CO_2-$_{eq}$/kg Product)	TATA Steel, 2012
Textiles[1]	Fabrics	12.5 (kg CO_2-$_{eq}$/kg Product)	TW, 2012
Paper & Cardboard[2]	Paper	800	ARJOWIGGINS, 2010
Fines[2]	Paper	800	ARJOWIGGINS, 2010

Notes:
[1] This is the direct footprint of manufacturing plants from yarn to customer, including spinning, dying, cutting and transport.
[2] Paper produced from virgin fibres.

6.2.2. Incineration Unit with Combined Heat and Power

Energy recovered from waste incineration was considered in this study. The SELCHP plant is located in London within the Borough of Lewisham, and is considered the major supplier of energy from waste (EfW) in the Capital. It operates an incineration unit (IU) based on the mass-burn process (see Section 2.5.2) and the company is generally recognised as the first EfW IU in the UK (SELCHP, 2010). The maximum capacity of the plant is reported to be 420,000 tpa of waste and the feed to the IU consists of co-mingled waste that originates from the Boroughs of Westminster, Bromley, Lewisham, Greenwich and a collection delivery from all of the GLA.

The electricity is generated using a 35 MW steam turbine generator, operating at a temperature of 395°C and a pressure of 46 bar. The electrical current is transformed to 132 kV for national grid exporting. The combined heat and power (CHP) plant was assumed to produce both electricity for the national grid and heat from the boiler system. The electrical generation was calculated for the CHP plant studied (Equation 6.3), as well as the heat generated by the CHP system (Equation 6.4, Zahari et al., 2010):

$$\text{EG (kWh/year)} = \eta_{elec}\left(\frac{\text{ITP}_i\,(\text{tpa})\times\text{HHV}_i\,(\text{kJ/kg})\times(1000\,\text{kg/tonne})}{3.6\,(\text{MJ/kWh})\times 1000\,(\text{kJ/MJ})}\right) \tag{6.3}$$

$$\text{HG (kWh/year)} = \left(\eta_{Heat} \Big/ \eta_{Boiler}\right)\times \left(\frac{\text{ITP}_i\,(\text{tpa})\times\text{HHV}_i\,(\text{kJ/kg})\times(1000\,\text{kg/tonne})}{3.6\,(\text{MJ/kWh})\times 1000\,(\text{kJ/MJ})}\right) \tag{6.4}$$

where ITP_i is the throughput of the component i (tpa), HHV_i is the higher heating value of component i, η_{elec} is the electrical generation efficiency of the unit, η_{Heat} is the heat generation efficiency of the unit and η_{Boiler} is the average efficiency of a domestic heat boiler in the UK. The formulation includes the conversion of the dimensions to obtain the electrical and heat generation in kWh per year. It was assumed that no glass, metal packaging, white goods or scrap metal (including aluminium) entered the IU feed stream. According to Finet (1987), the higher heating value (HHV) is the quantity of heat emitted during the complete combustion of 1 kg of MSW. The HHV numerical values for the different components in this analysis were taken as follows (Finet, 1987):

$HHV_{(1)}$ = 34500 kJ/kg - plastics
$HHV_{(2)}$ = 19500 kJ/kg - textiles
$HHV_{(3)}$ = 34500 kJ/kg - fines
$HHV_{(4)}$ = 16500 kJ/kg - paper and cardboard

$HHV_{(5)}$ = 18000 kJ/kg - organics

The electricity and heat generation efficiencies were taken for the standard CHP plant as reported by Murphy and McKeogh (2004): the value of η_{elec} was taken as 18%, whilst η_{Heat} equals 50%. The maximum seasonal efficiency of domestic boilers (η_{Boiler}) was taken in this study as 92% (EF, 2003).

Bottom ash is produced from incineration as a result of the combustion process and is the largest residue resulting from incineration processes. It differs in composition, but consists mainly of aggregate (80%), organics (5%) and other trace amounts (WMW, 2012), and it is used mainly in infrastructure projects (WMW, 2012). In Switzerland, bottom ash is mainly landfilled, however, in countries like Demark and Sweden it is used as road fillers (WMW, 2012). In this study, bottom ash was estimated as 20% of the IU throughput (Rand et al., 2000) and it was assumed to be split into two fractions. The first fraction (60% IBA produced) is sold as an aggregate, and the remainder is landfilled. This is a common practice through the EU25 countries and the assumption is based on the Gabi 5 software built-in incineration process which considers a similar practice for the IBA produced by incinerators (Gabi 5 DB V5.43, see Annex B). The fraction sold provides a source of revenue that credits the system developed. In this study, the IBA is credited by displacing the commercial processes otherwise required for aggregate production. According to Mitchell (2010), the carbon footprint of commercial aggregate production is equal to 34.4 kg CO_2/tonne, and this conversion factor was used in the analysis to credit the amount of aggregate (60% IBA) produced by the IU.

In order to calculate the amount of CO_2 emitted from the IU, the Gabi 5 software database was consulted to extract relevant conversion factors. In this study, the conversion factor used for the calculation of CO_2 emissions was 899.15 kg CO_2/tonne throughput (Gabi 5 DB V5.43), and the CO_2 emitted from the IU was considered as a direct burden in the final assessment of the system developed. The UK average electricity mix was used in this analysis to credit the electricity produced from the IU, and the average electricity mix conversion factor used was 0.05 kg CO_2/kWh, similar to the MRF station calculations (Gabi 5 DB V5.43). Marginal data were also used to credit the electricity produced. Each marginal data conversion factor corresponds to a combination number (Table 6.3), and this was utilised to compare between the different electricity off-setting options in order to determine the optimal environmental one. The marginal electricity conversion factors used were extracted from the Gabi 5 software, as reported in Table 6.8. The UK CCGT heat generation marginal value was used to off-set the heat production from the IU, where the heat is credited with 0.553 kg CO_2/ kWh, as previously reported by Staffell et al. (2012) in their UK study.

Table 6.8 Marginal Electricity Production Technology Conversion Factors in the UK Considered to Credit the Overall System Developed in this Work
Source: Gabi 5 Database (DB Version 5.43)

Power Source	kg $CO_{2\text{-}eq}$/ kWh (elec.)
Natural Gas	3×10^{-2}
Nuclear	4×10^{-4}
Hard Coal	8×10^{-2}
Wind	7×10^{-4}

6.2.3. Transfer Stations Considered

Generated waste from each individual point of origin (borough, city, etc.) is typically transferred to a large collection centre or a depot known as a transfer station (TS). This activity is considered as a part of the development of the system studied in this work. The location of these TSs is depicted (with respect to each borough) in Figure 6.7 and Table 6.9 summarises the distances between the TSs and the MRF and IU plant sites.

Table 6.9 Transfer Station (TS) Distances Considered in this Study

Borough	Transfer Station Name	Distance to MRF (miles)	Distances to IU (miles)
Greenwich	Re-use & Recycling Centre	3	8.5
Lewisham	Re-use & Recycling Centre	7.6	6.9
Exeter	Devon-Recycling Centre	211	204.1
Westminster	Cringle Dock Transfer Station	-	5.7
Bromley	Bromley- Civic Centre	-	9.2
GLA Collection to IU	-	-	15[1]

Notes:
[1] Assumed distance for the GLA collection to IU.

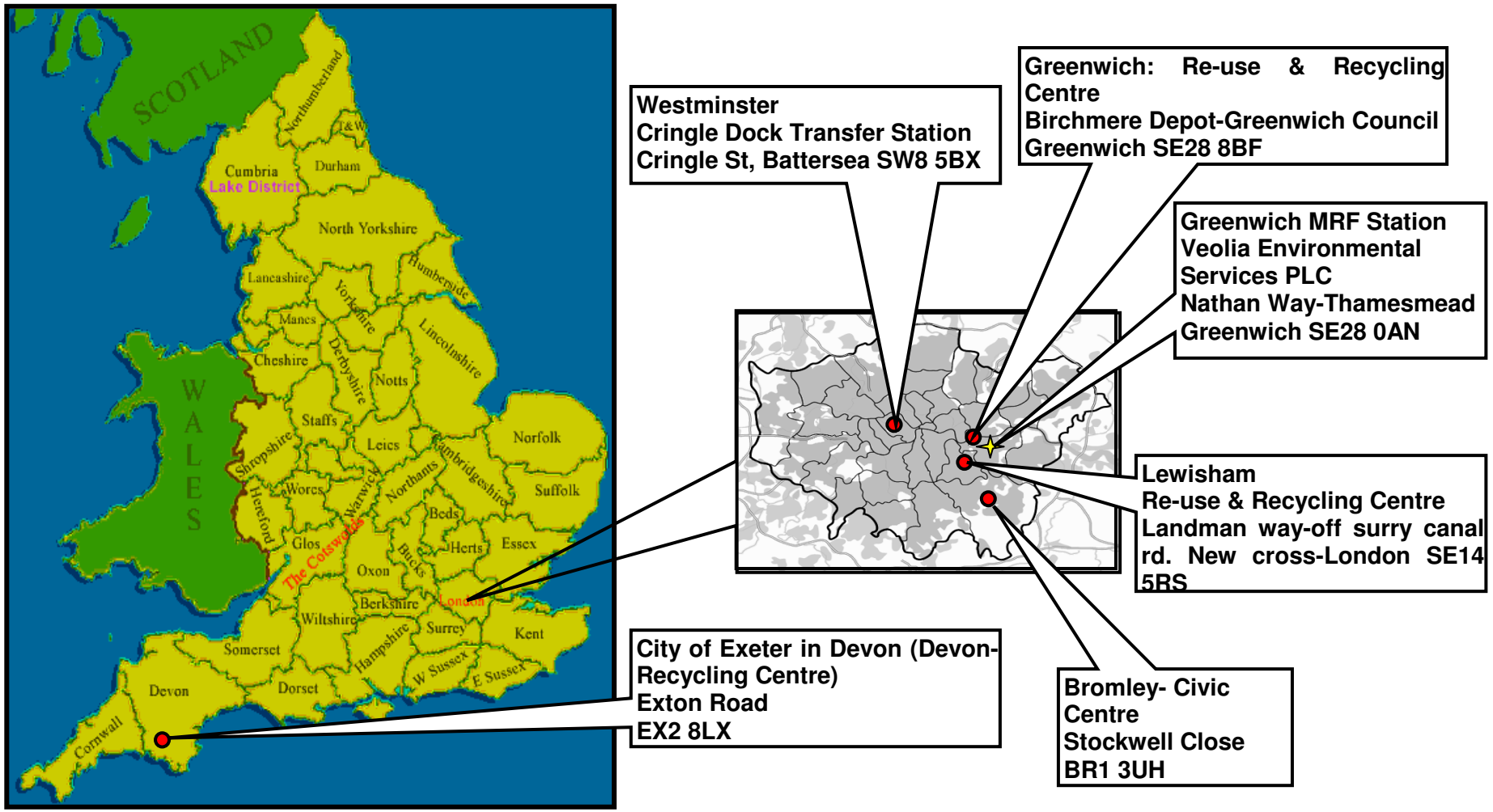

Figure 6.7 - Location of Recycling Centres and Boroughs Considered in the Study.

The TS diesel and electrical consumption for its processing line were calculated using Equations 6.5 and 6.6 (ADAS, 2008). Similar to the calculations for the MRF station, the carbon emission (kg CO_2/year) resulting from the transfer station (TS) processing line were evaluated using the conversion factor 2.68 kg CO_2/litre (UE, 2010).

$$\text{TSDC (litres)} = 0.47 \times \text{TSTP} \tag{6.5}$$

$$\text{EC (kWh)} = 1 \times \text{TSTP} \tag{6.6}$$

where TSDC is the total diesel consumed (litres) in the TS station, TSTP is total co-mingled throughput of the TS station processed in tpa and EC is the total electricity consumed in the MRF station (kWh). The UK average electricity grid mix was used in this analysis to off-set the CO_2 emitted from the electricity consumed in the TS (similar to the MRF). The conversion factor of 0.05 kg CO_2/kWh was used to calculate the emitted carbon dioxide from the TS stations (Gabi 5 DB V5.43), and is considered as a direct burden on the overall system developed.

6.2.4. Transport

The transportation distances vary between the different unit operations considered in this work (Table 6.9). Transportation contributes to the total environmental burden in terms of airborne pollutants and these include CO, NOx, PM_{10}, etc., CO_2 is also considered as a part of the transportation load activity. The contribution of CO_2 is the result of the diesel consumed by the trucks that transport the waste from the TSs to the MRF and the IU sites. The transportation burden is considered a direct emission that is added to the final GWP evaluation. It was assumed that each borough manages ten diesel engine trucks, which were assumed to have a capacity of 40 tonnes (maximum). Each truck operates with a maximum payload (40 tonnes), i.e. full capacity, as described by the Volvo Truck Co. (2008) and the number of trips required by each truck was calculated as shown in Equation 6.7.

$$\text{NTR} = \frac{\text{WG (tonnes/week)}}{\text{MPL (tonne/truck)} \times \text{NT (truck/week)}} \tag{6.7}$$

where NTR is the number of trips required for each truck to and from the TS, WG is the amount of waste transferred by each truck (tonne/week), MPL is the maximum truck payload (40 tonnes/truck) and NT is the number of trucks managed by each borough for TS activities (10 trucks/week).

The trucks operated were assumed to be of a long haul traffic-trailer type, with a fuel consumption of 0.53 l/km (0.85 l/mile, Volvo Truck Co., 2008). The diesel consumption was calculated for each round trip (Equation 6.8) and consequently for the number of trips required (NTR, Equation 6.9).

$$CD\,(\text{litres/week}) = di\,(\text{miles}) \times Cons\,(\text{litres/mile week}) \times 2 \quad (6.8)$$

$$DCT\,(\text{litres}) = NTR \times NT\,(\text{truck}) \times CD(\text{litres/truck}) \quad (6.9)$$

where NTR is the number of trips required for each truck to and from the transfer station, CD is the amount of diesel consumed (litres/week) for each truck in a round trip, Cons is the fuel consumption of the truck engine (0.85 litres/mile), DCT is the diesel consumed for the number of trips required (litres), and NT is the number of trucks (10 trucks). Equation 6.8 was multiplied by 2 to account for the each truck's round trip, i.e. to and from the TS.

In order to calculate the amount of CO and NOx emitted from the truck exhaust, the Euro 4 fuel category was assumed for the truck engine emissions (Volvo Truck Co., 2008) and the conversion factors were taken from the engine specifications described by Volvo Truck Co. (2008). The conversion factors used in this study were 13 g/litre for NOx and 1 g/litre for CO. NOx and CO contribute to the total GWP of the system studied and by obtaining the amount of CO and NOx which are released, the amount of CO_2-$_{eq}$ can be calculated by using the emission factors for NOx and CO, as reported by IPCC (2006). The amount of CO_2-$_{eq}$ resulting from the CO and NOx was calculated as follows:

$$NOx[kg_{CO_2-eq}] = \frac{DCT(\text{litres/year}) \times 13(\text{g NOx/litres}) \times 8(\text{kg } CO_{2-eq}/\text{kg NOx})}{1000(\text{g/kg})} \quad (6.10)$$

$$CO[kg_{CO_2-eq}] = \frac{DCT(\text{litres/year}) \times 1(\text{g CO/litres}) \times 3(\text{kg } CO_{2-eq}/\text{kg CO})}{1000(\text{g/kg})} \quad (6.11)$$

where DCT is the diesel consumed for the number of trips required (litres/year), NOx-$_{eq}$ is the emitted amount of NOx in terms of (kg $CO_{2\text{-}eq}$), CO-$_{eq}$ is the emitted amount of CO in terms of (kg $CO_{2\text{-}eq}$) and 8 (kg $CO_{2\text{-}eq}$/kg NOx) and 3 (kg $CO_{2\text{-}eq}$/kg CO) are the emission factors for converting the NOx and CO emission into CO_2-eq.

6.2.5. Thermo-Chemical Treatment Technologies Incorporated in the System Developed

In this study two TCT industrial technologies (the BP® LTP and VCC® hydrogenation processes) were incorporated in the overall system developed. In order to compare each technology with the conventional waste treatment routes employed in London, each TCT technology is assigned to a different scenario. The first scenario (baseline) includes the MRF and IU to reflect the current waste treatment route in London, the second includes the MRF, IU and the LTP process, while the third scenario includes the MRF, IU and VCC process. The feed to each TCT technology in scenarios 2 (LTP) and 3 (VCC) is assumed to be a fraction of the plastics recovered by the MRF. The following sections (6.2.5.1–6.2.5.2) describe the TCT units incorporated in this study in detail.

6.2.5.1. Low Temperature Pyrolysis Technology

The pyrolysis technology incorporated in this work is the BP® LTP or polymer cracking technology has been described previously by Tukker et al. (1999) and Perugini et al. (2005). This pyrolysis technology was commissioned by BP® in a pilot scale and is also known as BP cracking technology (Williams and Williams, 1999a, 1999b). The process accepts dry plastics as indicated by the feed criteria described in Table 6.10.

It was assumed that the unit receives a plastics feed of 1,000 tpa from the plastics produced by the Greenwich MRF station (Table 6.11), which mainly consists of polyolefins (PE+PP) (83%) (Tukker et al., 1999). It is very important to satisfy the chlorine content in the pyrolysis reactor by not exceeding the PVC amount being fed to the unit. The plastics breakdown previously shown in Table 6.2 was considered in this analysis to calculate the plastics breakdown.

Table 6.10 LTP Reactor Feed Criteria

Polymer Type Input	% of the Feed Mix	Amount Fed in this Study
Polyolefins (PE+PP)	> 83%	830 tpa
Polyvinyl Chloride (PVC)	< 2%	20 tpa
Polystyrene (PS)	<15%	150 tpa
Reminder Fraction Produced by MRF	-	8611 tpa

Table 6.11 MRF Plastics Throughput Break Down

Polymer Type Recovered	Amount (tpa)
Plastics throughput (MRF)	9611
Polyolefins (PE+PP)	5382
PVC	1807
PS	606
Reminder Fraction Produced by MRF	1817

Plastics (namely polyolefins) undergo a certain treatment, mainly concerned with size and chlorine content reduction, to meet with the requirements of the BP® polymer cracking (pyrolysis) process. Introducing a pyrolysis reactor provides the option of recovering a number of valuable chemicals (considered in this study), including rich gases and tars (heavy waxes and liquids). These chemicals can substitute a number of petrochemicals and in a consequential order include, propane (C_3) and butane (C_4), AR, naphtha and heat (energy) in the form of p-steam (Perugini et al., 2005).

Table 6.12 summarises the inputs and outputs of the BP LTP technology. The input materials were off-set to calculate their CO_2 contribution to the overall system and were considered as a direct burden. The products were also off-set and were considered as an avoided emission in this study. Table 6.12 also indicates the off-setting factors used in this study for the LTP process inputs and outputs considered.

Table 6.12 Summary of Inputs and Outputs Considered in this Study for the LTP Process and their Off-setting Factors.

Input Materials	Amount Required (Perugini et al., 2005)	Emission of Material	Notes	Reference
Sand	0.0085 kg/kg Feed	-	-	-
CaO	0.046 kg/kg Feed	-	-	-
Water	0.002 m^3/kg Feed	-	-	-
Naphtha	0.131 MJ/tonne Feed	1.3 (kg $CO_{2\text{-eq}}$/ kg Naphtha)	Direct Burden	Shell,2010
Electric energy	0.212 MJ/tonne Feed	0.05 (kg $CO_{2\text{-eq}}$/kWh)	UK Grid Mix.	Gabi 5
Output Products	**Amount Obtained**	**Emission of Product**	**Notes**	**Reference**
Gases (C_3-C_4)	0.147 kg/kg Feed	1.3 (kg $CO_{2\text{-eq}}$/ kg Naphtha)	Assumed to replace Naphtha	Shell,2010
Liquid (Naphtha)	0.265 MJ/kg Feed	1.3 (kg $CO_{2\text{-eq}}$/ kg Naphtha)	Avoided Burden	Shell,2010
Wax (AR)	0.448 kg/kg Feed	1.3 (kg $CO_{2\text{-eq}}$/ kg Naphtha)	Assumed to replace Naphtha	Shell,2010
CaO	0.04 kg/kg Feed	-	-	-
$CaCl_2$	0.077 kg/kg Feed	-	-	-
P- Steam (Heating)	1.48 MJ/kg Feed	0.533(kg $CO_{2\text{-eq}}$/ kWh)	UK CCGT	Staffell et al. (2012)
CO_2	0.345 kg/kg Feed	-	Avoided Burden	-
NOx	0.003 kg/kg Feed	8 (kg $CO_{2\text{-eq}}$/ kg NOx)	Emission Factor	IPCC (2006)
Sand & Coke	0.076 kg/kg Feed	-	Landfilled	
Waxy filter	0.046 kg/kg Feed	-	Landfilled	

6.2.5.2. Veba-Combi Cracking Hydrogenation

By definition, hydrogenation is the process of molecular cracking into highly reactive free radicals which are saturated with hydrogen as they form. The process integrated here and previously described by Tukker et al. (1999) is known as the VCC process. The main criterion of polyolefin feed is concerned with the PVC content (≤ 10%) and in this study the VCC unit has a PVC content of 10%. The feed in such processes is typically sent to a depolymerising unit to produce a light top product (consisting of 71 wt% $C5^{+}$, with a boiling range of 400°C and non-condensable (C_3-C_4) gases) and a heavy bottom product. The main product of this process is the syncrude produced, which can replace crude oil in a 1:1 ratio. The MRF throughput and plastics breakdown considered is similar to that for the LTP process (Table 6.11). The process is assumed to have a throughput feed of 1,000 tpa (again similar to the LTP process) and Table 6.13 summarises the process throughput and the plastics breakdown considered in this study. Table 6.14 shows the main input materials and chemicals produced by the VCC process and their off-setting values considered in this study.

Table 6.13 VCC Unit Feed Criteria

Polymer type	Amount (tpa)	%of the VCC Feed
Plastics Mix (VCC Feed)	1000	100
PO (PP+PE)	900	90
PVC	100	10
Reminder Fraction Produced by MRF	8611	-

Table 6.14 Summary of Inputs and Outputs Considered in this Study for the VCC Process and their Off-setting Factors.

Input Materials	Amount Required Perugini et al. (2005)	Emission of Material	Notes	Reference
Steam	0.112 MJ/kg Feed	0.533(kg $CO_{2\text{-eq}}$/ kWh)	UK CCGT	Staffell et al. (2012)
Electric energy	0.96 MJ/kg Feed	0.05 (kg $CO_{2\text{-eq}}$/ kWh)	UK Grid Mix.	Gabi 5
Natural gas	4.62 MJ/kg Feed	73.1(kg $CO_{2\text{-eq}}$/ mmBTU)		Felton et al. (2011)
CaO	0.001 kg/kg Feed	-	-	-
Hydrogen	0.011 kg/kg Feed	-	-	-
Output Products	**Amount Obtained**	**Emission of Product**	**Notes**	**Reference**
Syncrude (Crude Oil)	0.822 kg/kg Feed	0.43 (tonne CO_2/bbl)	Replacing Crude Oil Barrel Production	USEPA, 2012
E-gas (Natural Gas)	0.09 kg/kg Feed	73.1(kg $CO_{2\text{-eq}}$/ mmBTU)	Replacing Natural Gas Production	Felton et al. (2011)
HCl	0.005 kg/kg Feed	1100 (kg $CO_{2\text{-eq}}$/ tonne HCl)	Replacing Commercial HCl Production	Azapagic (2012)
$CaCl_2$	0.0041 kg/kg Feed	-	-	-
NH_3	0.006 gm/kg Feed	-	-	-
Hydrocarbons	2.23 gm/kg Feed	-	-	-
Solid waste	0.05 kg/kg Feed	-	Landfilled	-
CO_2	0.44 kg/kg Feed	-	Avoided Burden	-

6.2.6. Landfill

Few countries have reached a zero reliance on MSW landfill disposal. Sweden is a prime example, where household municipal and combustible wastes are strictly prohibited from being landfilled (Erikson et al., 2007), and countries like Germany, Belgium and France are approaching such a status, whilst in the UK, 50% of the waste is still landfilled. The Gabi 5 database (DB V5.43) reports the landfill sites existing in the EU_{25} countries, including those in the UK (see Annex C). The landfill model built into Gabi 5 is based on energy recovery, whereby the landfill gas is collected from and split into two fractions: the first is flared and the second one is fed to a CHP process.

In this study, the standard EU25 landfill model available within the Gabi 5 software was used to develop the landfill scenario. The landfilling burden value was taken as 533.4 (kg $CO_{2\text{-}eq}$/ tonne landfilled). In this work the landfill burden is considered as an avoided burden.

The transportation to the landfilling site was also accounted for in this study following the same approach as described in Section 6.2.4. The Basildon landfill site in Essex (SS16 4UW), is the closest to the IU and MRF and is approximately 36.4 miles from both sites. The fractions landfilled were assumed to be:

- 40% of the IBA produced by the IU (3,318 tpa) with CHP in all scenarios
- Waxy filter produced by the LTP process (46 tpa) in scenario 2
- Solids produced by the LTP process (200 tpa) in scenario 2
- Solid waste fraction (50 tpa) produced by the VCC hydrogenation (hydrocracking) process in scenario 3

6.3. Results and Discussion

Previous studies have indicated that the most significant impact categories for waste management are: the use of natural resources, energy turnover (energy output minus input) and GWP (Santoyo-Castelazo et al., 2012, Eriksson et al., 2007; Finndeven et al., 2005). In this section, the focus will be on the total energy turnover and GWP for the three scenarios studied. It is also important to note that the results presented below are often negative; this means that environmental interventions can be avoided and the studied scenario is credited. This argument strengthens the case for viewing waste as a resource rather than a burden on the urban environment, society and the industrial community.

6.3.1. Energy Use

Results for the energy consumed in each scenario are shown in Table 6.15. The energy consumed is the result of the energy input to the system studied, including utilities to the

different unit operations for the treatments and the TS. The energy demand for implementing TCT units in the form of a pyrolysis process (LTP) and a hydrogenation unit (VCC) did not increase the energy consumption of scenarios 2 and 3 by significant amount compared to the baseline scenario (scenario 1). Björklund and Finnveden (2005) reported in their LCA review of TCT options that such processes demand a higher energy consumption when compared to recycling and recovery processes. However in this study, both TCT units are relatively smaller in scale (1,000 tpa) than the MRF and the IU, which leads to a negligible increase in energy demand. Figure 6.8 shows the total energy turnover for the three scenarios studied.

Table 6.15 Energy consumed with Respect to the Studied Scenarios

Scenario No.	Treatment Option	Energy Consumed (kWh/year)
Scenario 1 (Baseline)	MRF+IU	4.68×10^6
Scenario 2	MRF+IU+LTP	4.68×10^6
Scenario 3	MRF+IU+VCC	4.68×10^6

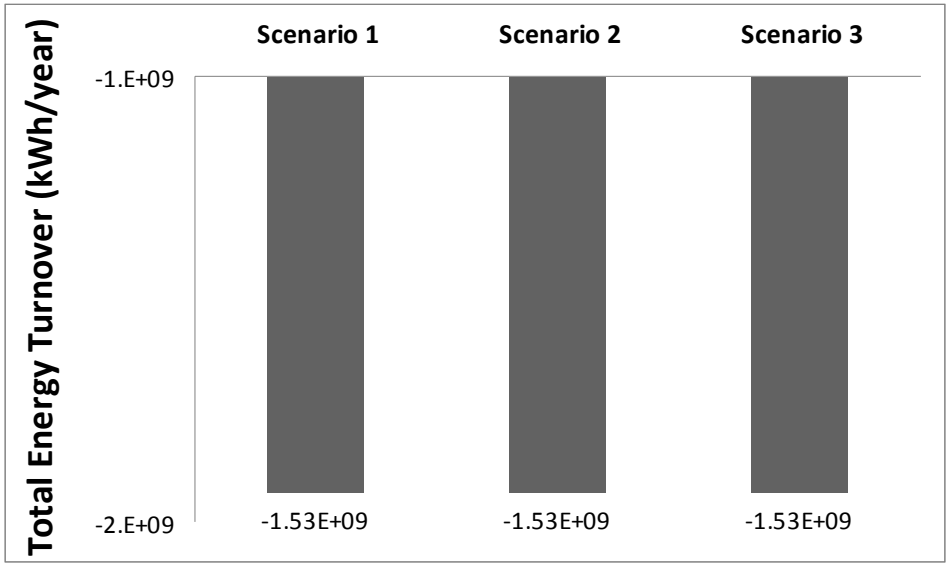

Figure 6.8 - Total Energy Turnover for the Three Studied Scenarios. Scenario 1: MRF+IU, Scenario 2: MRF+IU+LTP, Scenario 3: MRF+IU+VCC.

The energy turnover for all three scenarios is negative (Figure 6.8). This indicates that the energy output is larger than the energy input, which thereby credits all the scenarios in this study. Furthermore, the energy turnover was of the same order of magnitude in all the scenarios studied. The energy output of the LTP process is dependent on the plastics throughput which strengthens the argument for diverting more plastics towards pyrolysis in the GLA, resulting in the production of more clean energy. Scenario 2 (MRF+IU+LTP) did not demonstrate a significant increase in energy turnover due to the scale of the pyrolysis reactor (1,000 tpa) used.

6.3.2. Global Warming Potential

GWP is used for each scenario to analyse the carbon savings. These were noted previously and tabulated in a number of combinations with respect to the avoided electricity production process (Table 6.3). The ALCA in this study is combined with system expansion, which enables the assessment of the avoided burdens from the processes included in the overall system (Figure 6.2).

Figure 6.9 shows the GWP calculated for all the activities considered in scenario 1 with respect to the electricity avoided treatment. Combination 1 considers landfilling the total amount of the functional unit (552,141 tpa), whilst scenario 1 (combinations 2-6) includes the treatment of waste in the Greenwich MRF and the IU (CHP) of the SELCHP plant.

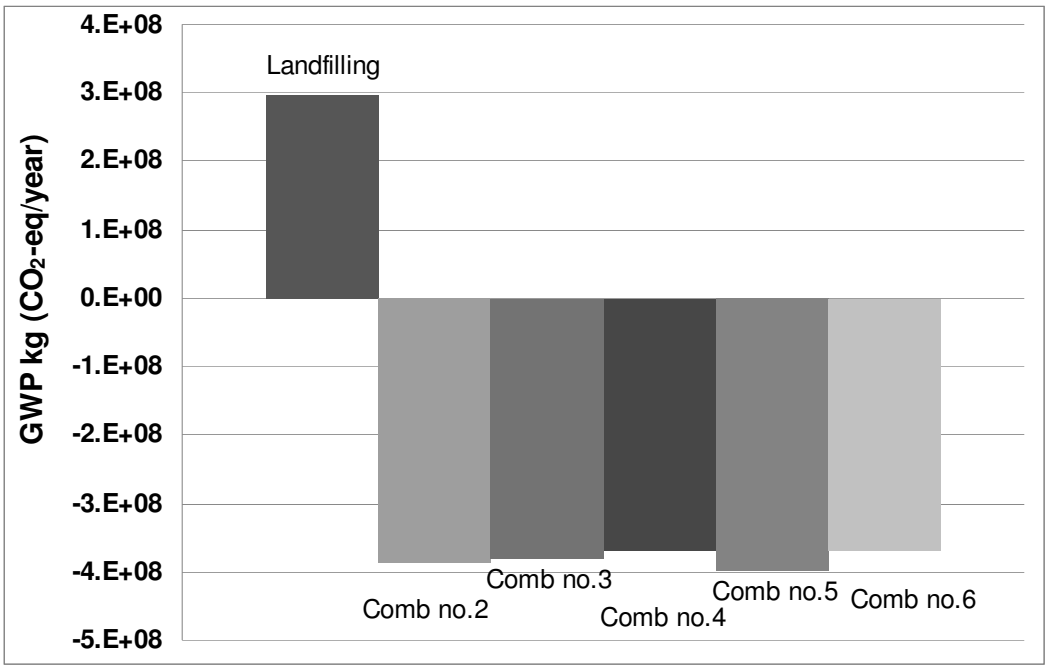

Figure 6.9 - GWP (kg $CO_{2\text{-eq}}$/year) for Combinations 2-6 Considering Scenario 1 (MRF+IU) for the Treatment of the Waste Including the Polymeric Fraction.

All the combinations studied for scenario 1 are negative, which indicates that all the treatments considered credit the scenario studied. Furthermore, combination 5 (avoided burden resulting from electricity produced from marginal hard coal technology) shows the optimal treatment of all combinations studied in scenario 1 (Figure 6.9). This is due to the fact that the hard coal off-setting conversion factor was the highest of all the avoided electricity treatment options (see Table 6.8). Higher avoided burden factors result in larger GWP savings (Erikson et al., 2007). Subsequently, scenarios 2 and 3 (implementing pyrolysis and hydrogenation, respectively) with hard coal electricity production gave the largest GWP savings (combinations 10 and 15, Figures 6.10-6.11).

Scenario 2 shows the largest carbon savings in comparison to the other two scenarios studied (Figure 6.10). This is due to larger amount of products being produced by the LTP process, which contributes to the total avoided burdens of this scenario. Products off-set for the BP LTP process included waxes (comparable to AR), gases (comparable to pentane (C_3) and butane (C_4) refinery cuts) and liquids (comparable to naphtha). These were all off-set with respect to commercial naphtha production. AR and both C_3 and C_4 refinery cuts are of crude oil refining origin, and were assumed to be of the same carbon footprint as the naphtha oil refining product. This assumption was made because of the lack of data for the carbon emission for AR and both C_3 and C_4 refinery cuts. Other off-set products for scenario 2 were heat (steam from LTP), CO_2 and NOx emitted from the process.

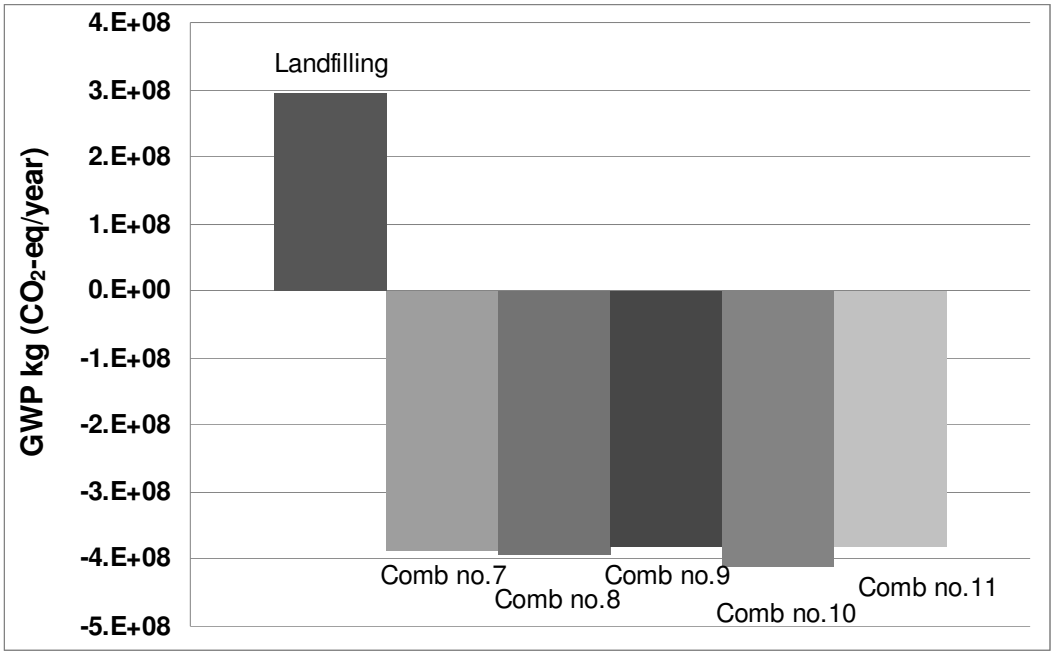

Figure 6.10 - GWP (kg $CO_{2\text{-eq}}$/year) for Combinations 7-11 Considering Scenario 2 (MRF+IU+LTP) for the treatment of the waste including the polymeric fraction.

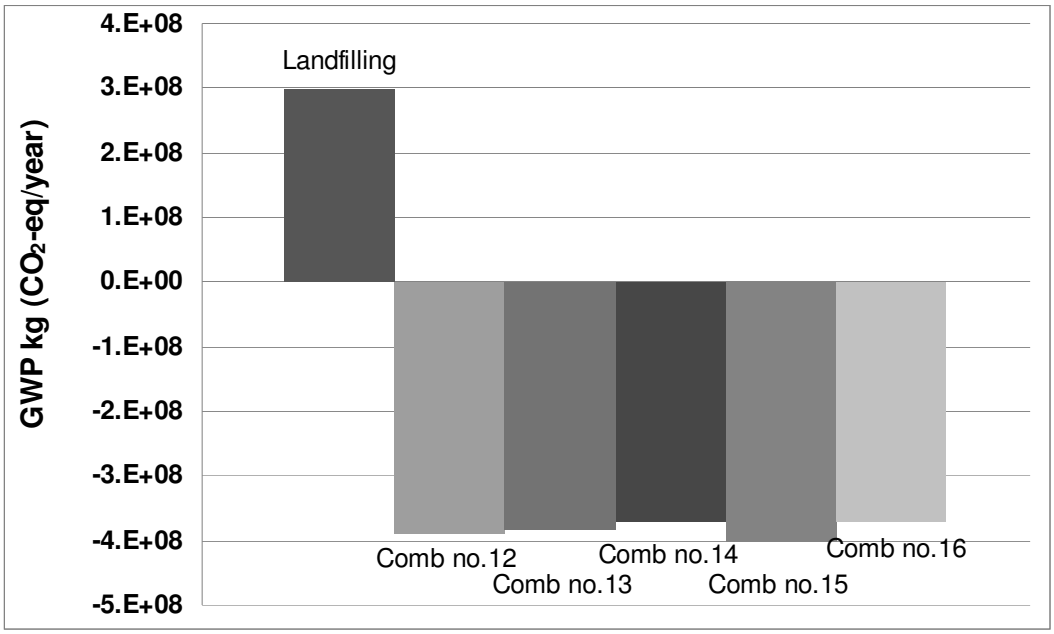

Figure 6.11 - GWP (kg $CO_{2\text{-eq}}$/year) for Combinations 12-16 Considering Scenario 3 (MRF+IU+VCC) for the treatment of the waste including the polymeric fraction.

Scenario 3 (Figure 6.11) shows further GWP savings when compared to the baseline scenario, i.e. scenario 1. Off-set (credited) products from the VCC included syncrude (comparable to crude oil), E-gas (comparable to natural gas) and HCl (replacing conventional HCl production), and the CO_2 emitted from the hydrocracker was considered as an avoided burden. All the scenarios studied had similar avoided treatments for the MRF and IU processes. Landfilling the waste resulting from the IU (40% IBA, all scenarios), the LTP process (waxy filter residue and solids, scenario 2) and the VCC process (solid waste from hydrocracker, scenario 3) were considered as an avoided treatment. Carbon emissions from the processing lines and electricity input to both the MRF and the five TSs, as well as the electricity input to the TCT units were considered as a direct burden on the system. Table 6.16 shows the GWP for all combinations with respect to each scenario considered and the electricity production processes.

Implementing the pyrolysis process (scenario 2) increases the overall GWP savings. By comparing the most environmentally friendly combination (combination 10, pyrolysis with electricity produced from hard coal) to combinations 5 and 15 (baseline and hydrogenation with electricity produced from hard coal, respectively), a 1.2×10^7 kg $CO_{2\text{-eq}}$ (compared to scenario 1) and 9×10^6 kg $CO_{2\text{-eq}}$ (compared to scenario 3) of GWP savings are achieved per year due to the implementation of the pyrolysis process. This indicates that pyrolysis is more preferable than PSW incineration and hydrogenation in terms of carbon savings.

Table 6.16 GWP (kg $CO_{2\text{-}eq}$/year) for all considered combinations in this study. Italic row indicates the least favourable of the system studied. Bold row indicates the most favourable of the system studied.

Combination	GWP (kg $CO_{2\text{-}eq}$/year) x10^8	Scenario Considered	Avoided Treatment for Electricity Production
1	2.97	Landfilling	Energy recovery in Landfill
2	-3.85	1 (MRF+IU)	UK Electricity Mix
3	-3.80	1 (MRF+IU)	UK Marginal Natural Gas
4	*-3.67*	*1 (MRF+IU)*	*UK Marginal Nuclear*
5	-3.97	1 (MRF+IU)	UK Marginal Hard Coal
6	-3.67	1 (MRF+IU)	UK Marginal Wind
7	-3.98	2 (MRF+IU+LTP)	UK Electricity Mix
8	-3.92	2 (MRF+IU+LTP)	UK Marginal Natural Gas
9	-3.80	2 (MRF+IU+LTP)	UK Marginal Nuclear
10	**-4.09**	**2 (MRF+IU+LTP)**	**UK Marginal Hard Coal**
11	-3.80	2 (MRF+IU+LTP)	UK Marginal Wind
12	-3.88	3 (MRF+IU+VCC)	UK Electricity Mix
13	-3.83	3 (MRF+IU+VCC)	UK Marginal Natural Gas
14	-3.70	3 (MRF+IU+VCC)	UK Marginal Nuclear
15	-4.00	3 (MRF+IU+VCC)	UK Marginal Hard Coal
16	-3.70	3 (MRF+IU+VCC)	UK Marginal Wind

6.3.3. Validation of Results using the Gabi 5 Software

A number of software packages exist and are available for LCA analysis and end-product development (see Section 5.5). In this work Gabi 5 was used to validate the work presented in Section 6.3.2. Gabi has been used in previous LCA studies investigating the waste management field (Tarantini et al., 2009; Luz et al., 2010; Santoyo-Castelazo et al., 2011). Gabi is marketed by PE Europe Co. and was developed in Germany by the University of Stuttgart. The software incorporates a database that includes a number of built-in processes and emission factors that benefit from industrial and applied research data (mainly from Europe). Scenario 1 was built-in the simulation environment of Gabi to verify the calculations performed numerically and check for discrepancies between both sets of results. The aim was to compare the values of GWP (expressed in kg $CO_{2\text{-}eq}$) obtained from the calculation performed in EXCEL with those obtained through Gabi 5.

6.3.4. Setting-up the Scenario in Gabi

The Gabi software used was of a version 5 with a database version of 5.43 (2012). Scenario 1 includes the following unit operations (see Figure 6.2-6.3):

- 5 TSs that transfer the co-mingled waste to the Greenwich MRF and to the IU located in the Borough of Lewisham (SELCHP). Details of the TSs and their throughputs were reported in Table 6.4 and the distances from the MRF and IU were reported in Table 6.9. Throughputs and distances were input in Gabi 5 for the scenario modelled and each transfer station was built as a separate auxiliary process. The utilities calculated from Equations 6.5-6.6.for each transfer station were entered into the software.

- The Greenwich MRF station processing 137,303 tpa of dry waste only was simulated in Gabi 5, with its throughput originating from three boroughs (Greenwich, Lewisham and City of Exeter). Figure 6.6 shows the feed breakdown for the different processes in the MRF. The MRF was built as an auxiliary process and figures for the utilities (electrical and diesel consumption, see Equations 6.1-6.2) where entered into the software.

- The IU model used by the Gabi software is for a European average waste to energy (WtE) plant, based on the treatment of average European MSW.

The IU model used by the Gabi 5 software considers a feed of homogenous waste throughput for a typical moving-grate, mass-burn incineration technology as used in Europe to meet the legal requirements set by the EU. The feed is assumed to be of a calorific value 0.06 GJ/tonne of MSW for electricity generation and the heat generation (in the form of steam) is based on 0.22 GJ/tonne of MSW fed to the IU. The software builds on industrial data gathered

from across Europe and does not calculate the electricity and heat generation based on the specific waste fractions in the throughput of the feed (as undertaken in this work, see Equations 6.3-6.4).

The GWP for one tonne of throughput is reported by Gabi 5 as 899.15 kg $CO_{2\text{-eq}}$, which was the figure used in the numerical calculations. This value includes the CO_2, NOx, CO and other contributors to the total CO_2 being emitted by the IU. Environmental impacts for waste collection, transport or any pre-treatment of the waste are not included in the data set for the built-in IU in Gabi. This is a similar assumption to that previously used when calculating in EXCEL. A schematic representation of the IU built-in model in the Gabi 5 software is given in Appendix C.

In Gabi 5, diesel used for transportation is modelled as a crude oil and bio components fuel supply production mix from a refinery (10 ppm sulphur, 5.75 wt% bio components). The amount of diesel in Gabi is entered as a weight (kg) and a diesel density of 0.832 kg/litre was used to convert the amounts entered. In addition, the UK grid mix was chosen to be modelled as the input electricity source to the units in the model.

The transportation activities in Gabi were modelled through the trucks managed for transporting the different waste fractions. The average truck emission category for the EU was chosen, which is based on the status of the January 2010 EU driving share code, with respect to a 1980 engine performance. The sulphur content of the diesel was declared in the database as 10 ppm, but the specific emissions of ammonia, benzene, carbon dioxide, carbon monoxide, methane, nitrogen monoxide, nitrogen dioxide, nitrous oxide, NMVOC, particulate $PM_{2.5}$, sulphur dioxide, were not given. However, the database literature shows that the GWP calculated in Gabi for transportation incorporates the above mentioned chemicals relevant to the GWP calculations. Input parameters for distances in (km) and payload (40 tonnes, as in the EXCEL calculations), where provided as inputs to the model (Table 6.9).

6.3.5. Results Obtained from Gabi Software

Figure 6.12 shows the whole system for scenario 1 as modelled in the Gabi 5 software. The different flow streams of the system were tracked, i.e. followed through the different processes, to account for the cradle to grave assessment of the technosphere (see values in Table 6.17).

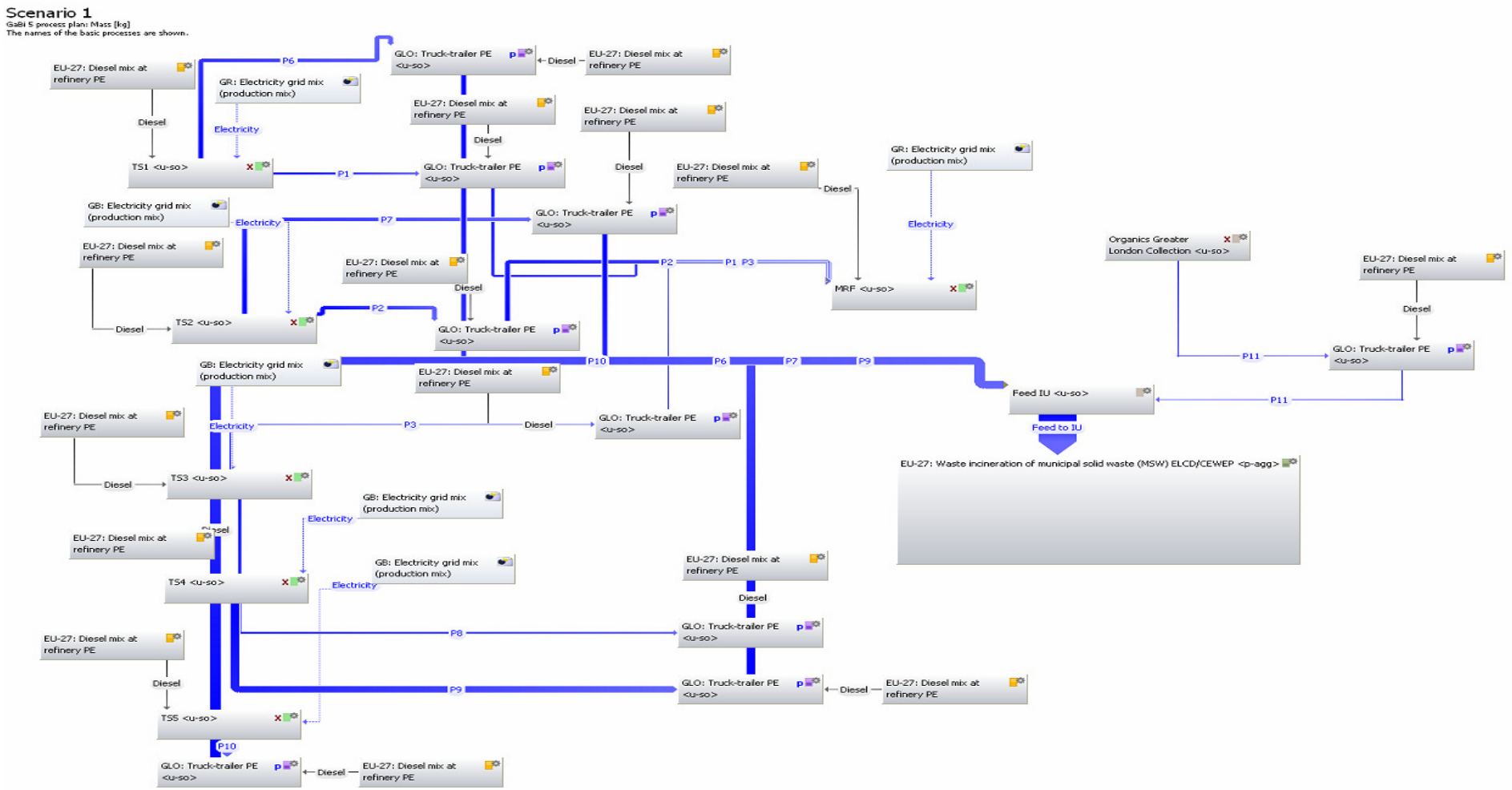

Figure 6.12 - Scenario 1 Modelled in Gabi 5 Software.

Table 6.17 Flows Modelled in the Gabi 5 Software for Scenario 1.

Point of Origin	Flow Name Fed to MRF	Flow Amount (tpa)	Flow Name Fed to IU	Flow Amount (tpa)
Greenwich	P1	50,686	P6	59,501
Lewisham	P2	59,566	P7	69,926
Exeter	P3	27,051	P8	31,755
Westminster	P4	-	P9	99,310
Bromley	P5	-	P10	124,346
GLA Collection	-	-	P11	30,000

The EXCEL calculations accounted for the different activities set within the boundaries of the scenario. The GWP of these activities are as follows:

- Transportation of IBA to the landfill site, which was calculated as described in Section 5.2.8. The GWP from this burden (including NOx and CO contribution to the transportation load) was equal to 1.8×10^5 kg $CO_{2\text{-eq}}$.
- The amount of GWP resulting from the combustion processes of the IU, which was equal to 3.7×10^8 kg $CO_{2\text{-eq}}$.
- Transportation activities to and from the MRF and IU from the five TSs, which amounted to 2.5×10^6 kg $CO_{2\text{-eq}}$.
- The MRF processing line and electricity input GWP contribution, which was calculated to be 8.3×10^5 kg $CO_{2\text{-eq}}$.
- The five TS processing lines and electricity input GWP contribution, which was calculated to be 7.3×10^5 kg $CO_{2\text{-eq}}$.

The total GWP calculated using EXCEL for scenario 1 in this study was equal to 3.77×10^8 kg $CO_{2\text{-eq}}$. Figure 6.13 shows the total GWP produced using the Gabi 5 simulated scenario 1, as well as the single GWP contribution of each element of the simulation (GWP from electricity input to MRF and TS, transportation by trucks to MRF and TS and the incineration process).

The total GWP calculated by Gabi 5 for the modelled case of scenario 1 is 3.74×10^8 kg $CO_{2\text{-eq}}$ (Figure 6.13). This results in a negligible discrepancy between the value obtained with EXCEL and the value produced by the software (<1% difference). This minor discrepancy results from the transportation element in the simulated case of scenario 1. The total transportation load calculated in EXCEL amounts to 2.7×10^6 kg $CO_{2\text{-eq}}$, however the results obtained using Gabi 5 show a value of 1.1×10^6 kg $CO_{2\text{-eq}}$ for the different transportation activities (see Figure 6.13, transportation trucks and rest). Gabi 5 implements the EU guidelines averaged across the whole continent, with truck trailers following the 1980 engine specification (including fuel consumption). Whilst in EXCEL calculations the truck engines where assumed to be of a Volvo truck long-haul type with consumed fuel at the rate of 0.53 l/km (Volvo Co., 2008).

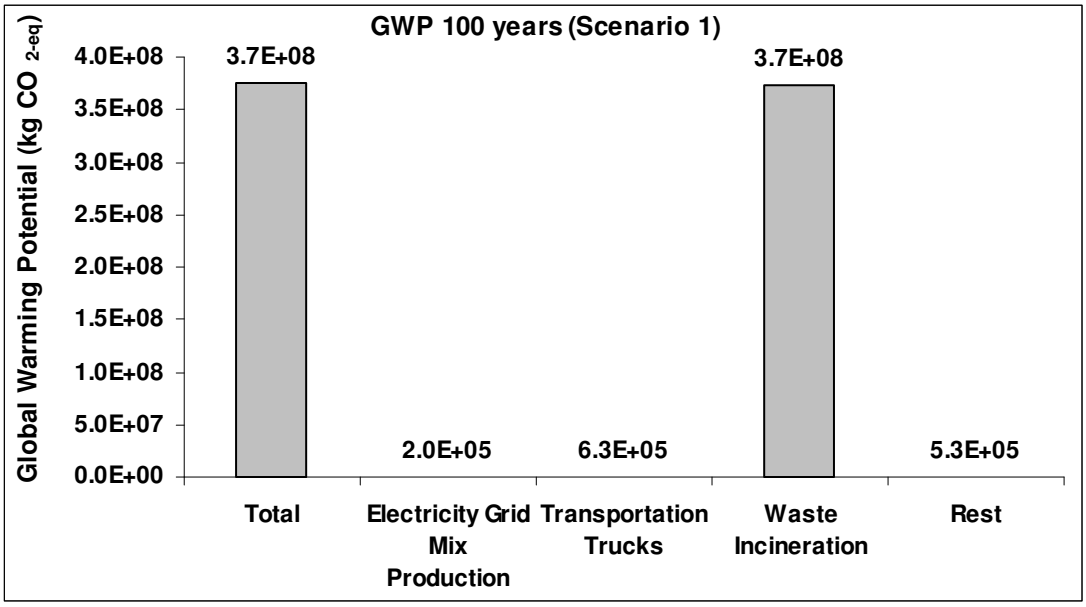

Figure 6.13 - GWP expressed in kg $CO_{2\text{-eq}}$ Calculated by the Gabi 5 software for Scenario 1.

The software calculates the electricity and heat generation based on the throughput of the waste incineration process, which resulted in different electrical and heat outputs from the IU, compared with the reported values in Section 6.3.1. The electrical and heat generated values from the IU calculated in EXCEL for all three scenarios were: 3.82×10^8 and 1.2×10^9 kWh/year, respectively, whereas the values produced by the software were 1.19×10^8 and 3.5×10^8 kWh/year, respectively. In assuming a homogenous mixture of feed with an average calorific value for all sorts of throughput, the IU output does not reflect the actual waste incineration for a specified case, thus demonstrating a disadvantage in relying on the software. In reality, waste is rarely constant in terms of calorific value as it originates from a number of sources and is the result of human activities that can change according to a number of socio-economic factors. The numerical calculations reflect a more realistic status for the waste fractions being treated in the IU and a more transparent overview of the processes considered (see Section 6.2.2.).

6.4. Techno-Economic Performance Assessment

The objective of this section is to investigate the economic viability of the overall system developed. The economic viability is assessed by determining costs and revenues for each scenario investigated. Capital costs (CC), operating and maintenance costs (OMC), transportation costs, collection costs, depreciation, corporation tax and gate fees are all included in this analysis. Governmental incentives, including Renewable Obligation Certificates (ROCs), Levy Exemption Certificates (LECs) and Packaging Recovery Notes (PRNs) were also included.

6.4.1. Capital Costs

Capital costs (CC) are defined as the capital sum needed to supply the necessary manufacturing and plant facilities (Patel et al., 2011). The scenarios developed in this study include the following unit operations: transfer stations (TSs), dry materials recovery facility (MRF) station, incineration unit (IU) plus a combined heat and power (CHP) plant, low temperature pyrolysis (LTP) unit and a VCC technology hydrogenation plant (Figure 6.2). Typical CC of mass-burn IUs (similar to the IU investigated in this work) are shown in Table 6.18 (DLD, 2002) with plant scales ranging from 50-500 ktpa.

Table 6.18 Capital Costs (CC) of Incineration Units (IU) in the UK with respect to Capacity. Source: DLD (2002)

Capacity Range (ktpa)	Capital Cost (£m)
50	16
100	28
150	41
200	47
400	87
500	93

Capital costs (CC) vary according to the plant scales. The Marshall and Swift (M&S) all-industry equipment index (formerly known as the Marshall and Stevens Index) is the most common index applied to correct (update) capital costs (CC) and operating and maintenance costs (OMC) (Stabert and Kundra, 2007). The Marshall and Swift (M&S) indices are developed for the US market but are used in this study for the UK on the studied scenarios. Table 6.19 shows the M&S indices used in Equation 6.12 to update the CC. Where cost data were unavailable, the sixth-tenth rule empirical correlation was used (Equation 6.13). The sixth-tenth rule has been recommended by Stabert and Kundra (2007) for scaling up or down equipment capacities, including capital and operating costs.

$$C_{Updated} = C_{Original} \times \left(\frac{I_{Updated}}{I_{Original}}\right) \quad (6.12)$$

$$PC = OC \times \left(\frac{DCp}{OCp}\right)^{n} \quad (6.13)$$

where $C_{updated}$ is the capital cost (CC) at the required time, $C_{Original}$ is the capital cost (CC) at the original cost time, $I_{Updated}$ is the M&S index at the updated required time, $I_{Original}$ is the M&S index at the original cost time, PC is the predicted cost, OC is the original cost, DCp is the desired capacity and OCp is the original capacity. The value of n was taken as 0.6 as recommended by Stabert and Kundra (2007).

Table 6.19 M&S Indices used in this work.
Source: Stabert and Kundra (2007)

M&S Index	Year
1061.9	1998
1104.2	2002
1468.6	2009

Table 6.20 shows the updated IU plant data used in this work. The IU plant investigated has a capacity of 420 ktpa, hence the updated capital cost (CC) is £119 m.

Table 6.20 Updated Capital Costs for the Incineration Unit used in this Study.

Capacity Range (ktpa)	Capital Cost (£m)	Updated Cost (£m)
50	16	21.3
100	28	37.2
150	41	54.5
200	47	62.5
400	87	115.7
500	93	123.7

Graham and Dougherty (2006) reported the costs of running a MRF plant in the UK processing up to 87,500 tpa. The average capital cost (CC) of a fully (dry) co-mingled MRF was reported to be £4.25 m (DLD, 2002). Using Equation 6.12, the updated average capital cost (CC) is calculated to be £5.65 m assuming the maximum capacity of 87,500 tpa. Consequently, different capital costs (CC) can be obtained for the dry MRF stations in the UK (Table 6.21). The MRF station in this study has a 146 ktpa capacity, which corresponds to a capital cost (CC) of £7.7 m.

Table 6.21 Updated Capital Costs for the MRF Stations in the UK used in this Study.

Unit Capacity (ktpa)	Capital Cost (£m)
87.5	5.6
100	6.1
146	7.7
150	7.8
200	9.3

The capital costs (CC) of the BP LTP process were reported by Tukker et al. (1999). These ranged between £15-20 m (average £17.5 m). By applying the M&S indices between the years 1998 and 2009 to update the average CC of the LTP process, a value of £24.2 m is obtained for a capacity of 25 ktpa. The capital costs (CC) shown in Table 6.22 were used in this work to obtain the capital cost (CC) of the LTP process.

Table 6.22 Updated Capital Costs for the LTP Process in the UK used in this Study.

Unit Capacity (ktpa)	Capital Cost (£m)	Unit Capacity (ktpa)	Capital Cost (£m)
5	9.21	50	36.68
10	13.97	75	46.79
15	17.81	80	48.63
20	21.17	100	55.60
25	24.20	125	63.57
30	27.00	150	70.92

The capital cost (CC) for the hydrocracking unit was taken from pyrolysis/gasification plants category, as described by DLD (2002). Similar to the IU, MRF and LTP processes, the average CC were updated using the M&S indices for different plant capacities. Table 6.23 shows the CC for the VCC hydrocracking process used in this study.

Table 6.23 Updated Capital Costs for the VCC Process in the UK used in this Study.

Unit Capacity (ktpa)	Capital Cost (£m)	Unit Capacity (ktpa)	Capital Cost (£m)
5	11.13	50	44.31
10	16.87	75	56.52
15	21.52	80	58.75
20	25.57	100	67.17
25	29.24	125	76.79
30	32.62	150	85.66

The capital costs (CC) of the five transfer stations (TS) were also considered. The capacity of each TS differs based on the population of the borough it serves. Dirty MRF stations perform a similar function to TS (see Section 2.2.1) and CC for TS were taken from DLD (2002) for dirty MRF stations. Table 6.24 shows the CC updated using the M&S indices.

Table 6.24 Updated Capital Costs for the Transfer Stations (TS) used in this Study.

Unit Capacity (tpa)	Capital Cost (£m)
60,000	8.8
100,000	11.97
110,000	12.67
120,000	13.35
130,000	14.01

6.4.2. Capital Recovery Factor & Interest Rate

A capital recovery factor (CRF) is defined as the ratio of a constant annuity to the present value of receiving that annuity for a length of time. Using Equation 6.14 the CRF was calculated for this work. The CRF is applied to the CC of each unit in order to account for the total project life time (assumed to be 20 years) and the interest rate (taken to be 7.5% for the UK market). Therefore, the capital costs (CC) for the units in each scenario are calculated using Equation 6.15.

$$CRF = \frac{ir}{1-(\frac{1}{(1+ir)^{m}})} \quad (6.14)$$

$$CC_{a} = CRF \times CC_{C\,i} \quad (6.15)$$

where CRF is the capital recovery factor calculated to be 0.09 in this work, ir is the interest rate which is assumed to be 7.5%, m is the project life time taken as 20 years, CC_a is the actual CC used in the final economic assessment in this work for unit i and $CC_{C\,i}$ is the updated capital cost of unit i (see Section 6.4.3).

6.4.3. Collection, Running, Operating & Maintenance Costs and Gate Fees

Gate fees are costs that off-set the different operating and running costs of a plant (Yassin, 2007). In this study, the MRF gate fee is considered as a running cost for the Greenwich MRF station. Plastics handled in a TCT facility will divert the amount processed from landfilling (or other processes) and hence the gate fees of such facilities (i.e. LTP and VCC) are taken as revenue.

The different boroughs investigated in this study house a varied population and each borough council is responsible for setting up the collection for each household. This typically includes four box bags individually assigned to: organics, paper and cardboard, mixed glass and tinfoil and plastics (Didsbury, 2006). A running collection cost is also part of the collection costs of each borough's annual budget. A set-up cost of £45 per household per year and a running cost £2.30 per household per year were considered in this study (Didsbury, 2006). Table 6.25 shows the collection costs for each borough considered in this study, with a breakdown of the box bags assumed to contain the co-mingled waste collected.

Table 6.25 Collection Cost Breakdown with Respect to Each Borough Number of Households.

Borough	Greenwich (B1)	Lewisham (B2)	Exeter (B3)	Westminster (B4)	Bromley (B5)
No. Households (ONS, 2009)	92,788	107,412	46,573	91,172	125,866
Box Bag no.1 Organics	59,501	69,926	31,755	63,091	789,96
Box Bag no.2 P & C	26,445	31,078	14,113	28,040	35,109
Box Bag no.3 Mixed Glass	77,13	9,064	4,116	81,78	10,240
Box Bag no.4 Plastics & Tinfoil	16,528	19,424	8,821	17,525	21,943
Total TS Feed (tpa)	110,187	129,492	58,806	116,835	146,288
Setting up Cost (£)	4,175,460	4,833,540	209,5785	410,2740	5,663,970
Running Cost (£/year)	213,412	247,048	107,118	209,696	289,492
Total Collection Cost (£/yr)	4,388,872	5,080,588	2,202,903	4,312,436	595,3462

Other running costs, OMC and gate fees involved in this study are described as follows:

- TS running costs: £47.73 per tonne throughput was used for each of the five TSs (ADAS, 2008).
- MRF gate fee: £30 per tonne throughput for the Greenwich MRF (Graham & Dougherty, 2006; Graham, 2009).
- IU OMC: £40 per tonne (DLD, 2002).
- Landfill gate fees: £33 per tonne throughput in each scenario (HE EPI).
- Transportation standing charges: standing charges (per year) for the different transportation activities of the trucks managed included (per truck per year): road tax (£245), insurance (£1,020), depreciation (£4,737) and breakdown cover (£50) (AA, 2010).
- Transportation running costs: running costs for trucks managed (per year) included (per truck per year): tyres (£0.021), service labour cost (£0.0323), replacement parts (£0.0312), truck driver salary (£24,000), two loader salaries (£21,000 per loader) and the diesel cost (UK average for 2010, £1.213 per litre) (WRAP 2009; AA, 2010).

6.4.4. Projected Revenues

Projected revenues for each scenario depend on the sales of electricity, heat, chemicals and petrochemicals produced by the thermo-chemical treatment (TCT) units, governmental incentives in the UK including renewable obligation certificates (ROCs), levy exemption certificates (LECs) and packaging recovery notes (PRNs) and sales of aggregate from the incineration bottom ash (IBA) recovered. The different revenues considered are described as follows:

- BP LTP process gate fee: £172 per tonne throughput for the pyrolysis process (scenario 2) (Tukker et al., 1999).
- VCC unit gate fee: £220 per tonne throughput for the hydrocracking process (scenario 3) (Tukker et al., 1999).
- Sales of electricity: the UK standard price of £0.188/ kWh was assumed (UK energy, 2010).
- Sales of heat: the heat produced from the IU (all scenarios) and LTP process (scenario 2) was sold at a price of £0.039/ kWh (BEC, 2010).
- Renewable Obligation Certificates (ROCs): a value of £38.69/kWh was used, which is the reported price of ROCs in 2011 (Ofgem, 2011). This is a UK Governmental incentive provided for IU produced energy (Electricity only). According to the

ROCs banding table published by the department of energy and climate change (DECC) in 2012, pyrolysis receives 2 ROC/kWh for electricity production. Hence, no ROCs are received by the BP process in scenario 2 (heat production only in the form of p-steam).

- Levy Exemption Certificates (LECs): this represents the exemption value for the climate change levy on energy for CHP plants in the UK. The rate used is £4.56/kWh electricity. (Inenco, 2010).
- Packaging Recovery Notes (PRNs): these are part of the UK producers' responsibility requirements as introduced in 1994. PRNs are defined as a type of document that provides evidence that waste packaging material that has been recycled into a new product. The profit from PRN sales is included in the total profits of each scenario. PRNs are given to the recovered products from a MRF station and a PRN is granted for each tonne of packaging material that has been recovered and recycled. PRNs considered in this study were for glass (£3.93/PRN, assuming 50% is recovered for packaging uses), plastics (£10.667/PRN, 4% only, which is the dense plastics content, Waste Watch, 2003) and steel (£6.208/PRN, considered in this study as metal packaging and white goods/and scrap metals). These prices were taken from Letsrecycle (2010) for the average prices between January and June of 2011.
- Sales of aggregate: the price for IBA recovered from the IU (60% of the recovered fraction was assumed to be sold as aggregate) was taken from WMW (2012) for aggregate (£3.5/tonne).
- Sales of MRF recovered products: recovered products from the Greenwich MRF station (in all three scenarios) were assumed to be sold at the price of recovered waste fractions (Table 6.26). It was assumed in this work that the extracted amount of plastics for the TCT units feed in scenario 2 and 3 will not affect the price of the plastic fraction sold by the MRF station.
- Sales of chemicals and petrochemicals produced by the TCT units: prices for equivalent products produced by the TCT units (LTP in scenario 2 and VCC in scenario 3) are reported in Table 6.27. The products are all valuable chemicals that compete in the international market and make TCT an attractive recovery route.

Table 6.26 Prices of dry fractions of waste, virgin and recycled polymers.

Item	Price (£/tonne)*	Notes
Plastic	30.4	Mixed Plastics***
Textiles	-	N/A
Glass	4.00	Mixed culet glass price**
Metal pack	124.10	Price for metals***
White goods/scrap metals	124.10	Price for metals***
Fines	5.00	Price for wood taken form *Letsrecycle.com* for Oct 2010
Paper and cardboard	15.50	Price for paper***

*** (1 € = £ 0.88)**
**** taken form www.wrap.org.uk/recycling_industry/market_information/market_knowledge**
***** taken from Economopoulos (2010).**

Table 6.27 Thermo-Chemical Treatment (TCT) units main products and their prices.

Unit	Main Products/PC Replacement or Equivalents	Price[1]	Avg. Price[2]
LT Pyrolysis Process	Gas fraction/C_3-C_4 Refinery Cut+	515.99 (C_3) ($/T) 521.95 ($C_4$) ($/T)	2002-2010 2002-2010
	Waxes/AR+	162.84 (AR) ($/T)	2000-2002
	Liquids/Naphtha+	458.13 (Nap) ($/T)	2000-2010
	CaO-$CaCl_2$	CaO[3] (190$/tonne)	-
Hydrocracking Process	E-Gas (fraction)/Natural Gas+	5.97 (NG) ($/mmBTU)	2000-2010
	Syncrude/Crude Oil+	52.35 (Brent) ($/bbl)	2000-2010
	Solid Residues	-	
	$CaCl_2$	199 $/tonne [4]	

Note:
***Products marked with (+) indicate their inclusion as an avoided burden in this study.**
[1]Personal communication with Eng. Ayyed Al-Fadhlee, Kuwait Petroleum Cooperation (KPC). Tel: +965-24993037, email: ayf@kpc.com.kw
[2] Average prices between these years, except 2010 up to July.
[3] Taken from: alibaba.com
[4] (1.54 = £ 1)

The annual total profit for each scenario is calculated (before taxation) as:

$$TP = \sum Cost_r - PR \qquad (6.16)$$

where TP is the annual project profit including CC and running costs in the first year (£), $\sum Cost_r$ is the total running, gate fees and OMC of all units in the project (£) and PR is the projected revenue from the total sales of the project (£). Consequently, if the project is in deficit (not profitable), then the outcome of Equation 6.16 will be positive.

6.4.5. Corporation Tax

Corporation tax is applied on the projects taxable profits (Patel et al., 2011).[1] The amount of

[1] Products from EfW schemes are exempted from other taxes in the UK including carbon tax. Personal Communication with Ms. Chandini Patel, Ofgem, UK.

corporation tax payable is calculated according to the following equation:

$$CT = [(Ptp + Dpn) - Ca)] \times TR \quad (6.17)$$

where CT is the corporation tax payable (£), Ptp is the pre-tax profits from sales over the project life span (£), Dpn is the annual straight line depreciation charge (£), Ca is the capital allowances replacing the depreciation charges and taken as £25,000 per annum (HMR&C, 2009; 2012), and TR is the tax rate on profits taken as 28% (Patel et al., 2011).

The depreciation (Dpn) considers the project's need for investment over the life span of the project in a way that reflects its reducing value (Patel et al., 2011). Equation 6.18 shows the formula used in this study to calculate the Dpn.

$$Dpn = {C - R}/{N} \quad (6.18)$$

where C is the investment cost taken as the total CC calculated in Equation 6.15 (£), R is the residual value of the asset taken as 10% of the investment cost (C) and N is the project life span (years).

In this work, the profitability of each scenario is determined by comparing the net present value (NPV) and the internal rate of return (IRR). NPV and IRR are standardized financial tools to assess the profitability of projects. A scenario is economically attractive if it has the highest IRR and the NPV is greater than zero (Yassin et al, 2009, Patel et al., 2011). The NVP is an indicator of how much value the project adds to the investment and refers to the present values of all costs and associated revenues and is calculated according to Equation 6.19 (Yassin et al, 2009, Patel et al., 2011).

$$NPV = \sum_{n=1}^{20} \frac{CF_n}{(1+i)^n} - TPC \quad (6.19)$$

where NPV is the net present value (£), CF_n is the annual cash flow (revenues – operating costs) (£), i is the discount rate taken as 6% for the UK market (Patel et al., 2011) and TPC is the total plant cost (£). The IRR is calculated as the discount rate that makes the NPV equal to zero using the IRR function in Microsoft EXCEL (Yassin et al, 2009, Patel et al., 2011)

6.5. Economic Performance

The economic performance of all three scenarios is summarised in Table 6.28 where the capital cost (CC) and operating and maintenance cost (OMC) are reported for each scenario. Running costs for each scenario includes transportation, collection and operating and maintenance. Pre-tax annual profits (£/yr), net present value (£) and internal rate of return (%) for the entire duration of the scenarios life (20 years), are also reported. In addition to the results of the scenarios developed and discussed in Section 6.2, results of the addition of 1 ktpa units of LTP and VCC to each scenario are reported. Four LTP reactors were added to scenario 2 (Pyrolysis) and five to scenario 3 (hydrocracking) to cover the maximum amount of available plastics and reactor feed criteria in each scenario (see Sections 6.2.5.1-6.2.5.2). Moreover, results of adding 50, 100 and 150 ktpa units of LTP and VCC were included, assuming the same reactor feed criteria and the availability of treatable plastics from elsewhere. This was performed to investigate the impact of thermo-chemical treatment (TCT) unit capacity on net present value (NPV) and internal rate of return (IRR) with a similar order of magnitude to the capacity of the MRF and IU in the studied system.

The results show that hydrogenation represents the most expensive option due to the higher capital cost it requires, ranging from £12.8 m to £21 m for the studied scenarios (Table 6.28). In contrast, the cheapest option is always the non thermo-chemical scenarios (MRF+IU), with no additional running and capital costs of either pyrolysis or hydrocracking reactors. Therefore, thermo-chemical treatment (TCT) units, namely LTP and VCC, need to project a very high revenue to overcome the additional CC they impose. There were no noticeable differences in NPV and IRR using the maximum treatable plastics in the studied scenarios, i.e. with the addition of 1 to 5 ktpa VCC units or 1 to 4 ktpa LTP units.

The gate fees for both thermo-chemical treatment (TCT) plants (LTP and VCC) represent an additional profit in the range of £0.17 to 26 m for LTP and £0.22 to 33m for the VCC, depending on the capacity considered. However, the corporation tax (CT) which is dependent on pre-tax profit and capital costs (CC) is highest in scenarios with hydrocracking. This is due to the higher pre-tax profits and CC of scenario 3 (hydrocracking) compared to scenarios 1 and 2 (pyrolysis) over the scenario's lifetime. In fact, there were no noticeable differences in NPV and IRR up to the point of introducing a 50 ktpa of either a pyrolysis or hydrocracking unit to the baseline scenario (MRF+IU) (see Table 6.28). A 96% increase in pre-tax annual profit (TP) is calculated for the 150 ktpa VCC unit addition to the base scenario (MRF+IU). Furthermore, a 19% increase in corporation tax is also reported for the addition of the 150 ktpa VCC unit due to higher profits. Moreover, the hydrocracking scenario studied at 150 ktpa shows the highest net present value (NPV) and internal rate of return (IRR). This is due to the high profits it projects

from the hydrocracking product sales which overcomes all its costs and results in an increase of in NPV by 98% and in IRR by 60% compared to the baseline scenario (MRF+IU). The addition of the LTP unit was also profitable at scales exceeding 50 ktpa (Table 6.28). However, the profitability from the VCC hydrogenation sales exceeded the ones generated from the LTP process due to product sales and prices (see Table 6.27).

Table 6.28 Economic Performance of the Scenarios Studied.

	MRF+IU	MRF+IU +LTP(1ktpa)	MRF+IU +VCC (1ktpa)	MRF+IU +LTP (2ktpa)	MRF+IU +VCC (2ktpa)	MRF+IU +LTP (3ktpa)	MRF+IU +VCC (3ktpa)
Total Capital Cost (£m/yr)	12.4	12.7	12.8	13.1	13.2	13.4	13.6
Project Life (years)	20	20	20	20	20	20	20
Collection Cost (£m/yr)	22	22	22	22	22	22	22
MRF Gate Fee (£m/yr)	4.1	4.1	4.1	4.1	4.1	4.1	4.1
TS Running Cost (£m/yr)	26.8	26.8	26.8	26.8	26.8	26.8	26.8
Transportation Cost (£m/yr)	4.3	4.3	4.3	4.3	4.3	4.3	4.3
Landfill Gate fees (£m/yr)	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Landfill Transportation Cost (£m/yr)	0.72	0.72	0.72	0.72	0.72	0.72	0.72
IU O&M Cost (£m/yr)	18.7	18.7	18.7	18.7	18.7	18.7	18.7
LTP Gate Fees (£m/yr)	-	0.17	-	0.34	-	0.51	-
VCC Gate Fees (£m/yr)	-	-	0.22	-	0.44	-	0.66
IU Sales (£m/yr)	117	117	117	117	117	117	117
IBA Sales (£m/yr)	0.17	0.17	0.17	0.17	0.17	0.17	0.17
MRF Sales (£m/yr)	2.1	2.1	2.1	2.03	2.03	2.0	2.0
LEC Sales (£m/yr)	1.7	1.7	1.7	1.7	1.7	1.7	1.7
ROC Sales (£m/yr)	14.8	14.8	14.8	14.8	14.8	14.8	14.8
PRN Sales (£m/yr)	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Pre-tax Annual Profit[1] (£m/yr)	-58	-58.3	-58.1	-58.5	-58	-58.8	-58.1
Corporation Tax (£m)	759	760.3	760.8	760.9	761.9	761.4	763.1
IRR (%)	33	33	33	33	33	33	33
NPV (£m)	630.2	632.7	630.1	635.3	629.1	637.8	628.9
NPV (£/tonne)	57.1	57.3	57.1	57.5	57	58	57

Notes: [1]Calculated from Equation 6.16. The negative sign indicates that the project is in profit.

Table 6.28 (Cont'd) Economic Performance of the Scenarios Studied.

	MRF+IU +LTP(4ktpa)	MRF+IU +VCC (4ktpa)	MRF+IU +VCC (5ktpa)	MRF+IU +LTP (4ktpa)[2]	MRF+IU +VCC (5ktpa)[2]
Total Capital Cost (£m/yr)	13.4	14.1	14.5	13.1	14.1
Project Life (years)	20	20	20	20	20
Collection Cost (£m/yr)	22	22	22	22	22
MRF Gate Fee (£m/yr)	4.1	4.1	4.1	4.1	4.1
TS Running Cost (£m/yr)	26.8	26.8	26.8	26.8	26.8
Transportation Cost (£m/yr)	4.3	4.3	4.3	4.3	4.3
Landfill Gate fees (£m/yr)	1.1	1.1	1.1	1.1	1.1
Landfill Transportation Cost (£m/yr)	0.72	0.72	0.72	0.72	0.72
IU O&M Cost (£m/yr)	18.7	18.7	18.7	18.7	18.7
LTP Gate Fees (£m/yr)	0.68	-	-	0.68	-
VCC Gate Fees (£m/yr)	-	0.88	1.1	-	1.1
IU Sales (£m/yr)	117	117	117	117	117
IBA Sales (£m/yr)	0.17	0.17	0.17	0.17	0.17
MRF Sales (£m/yr)	2.1	2.1	2.1	2.1	2.1
LEC Sales (£m/yr)	1.7	1.7	1.7	1.7	1.7
ROC Sales (£m/yr)	14.8	14.8	14.8	14.8	14.8
PRN Sales (£m/yr)	0.12	0.12	0.12	0.12	0.12
Pre-tax Annual Profit[1] (£m/yr)	-59.1	-58	-58	-59.1	-58.3
CT Payable over 20 years (£m)	762.2	764	765.1	762	765.1
IRR (%)	33	33	32	33	33
NPV (£m)	641.1	628.1	627.5	641	632.6
NPV (£/tonne)	58	57	57	58	57

Notes: [1]Calculated from Equation 6.16. The negative sign indicates that the project is in profit.
[2]Upscaled at the capital cost to maximum allowable feed of plastics.

Table 6.28 (Cont'd) Economic Performance of the Scenarios Studied.

	MRF+IU +LTP (50ktpa)	MRF+IU +VCC (50ktpa)	MRF+IU +LTP (100ktpa)	MRF+IU +VCC (100ktpa)	MRF+IU +LTP (150ktpa)	MRF+IU +VCC (150ktpa)
Total Capital Cost (£m/yr)	16	16.7	17.8	17.8	19.3	21
Project Life (years)	20	20	20	20	20	20
Collection Cost (£m/yr)	22	22	22	22	22	22
MRF Gate Fee (£m/yr)	4.1	4.1	4.1	4.1	4.1	4.1
TS Running Cost (£m/yr)	26.8	26.8	26.8	26.8	26.8	26.8
Transportation Cost (£m/yr)	4.3	4.3	4.3	4.3	4.3	4.3
Landfill Gate fees (£m/yr)	1.1	1.1	1.1	1.1	1.1	1.1
Landfill Transportation Cost (£m/yr)	0.72	0.72	0.72	0.72	0.72	0.72
IU O&M Cost (£m/yr)	18.7	18.7	18.7	18.7	18.7	18.7
LTP Gate Fees (£m/yr)	8.6	-	17.2	-	26	-
VCC Gate Fees (£m/yr)	-	11	-	22	-	33
IU Sales (£m/yr)	117	117	117	117	117	117
IBA Sales (£m/yr)	0.17	0.17	0.17	0.17	0.17	0.17
MRF Sales (£m/yr)	2.1	2.1	2.1	2.1	2.1	2.1
LEC Sales (£m/yr)	1.7	1.7	1.7	1.7	1.7	1.7
ROC Sales (£m/yr)	14.8	14.8	14.8	14.8	14.8	14.8
PRN Sales (£m/yr)	0.12	0.12	0.12	0.12	0.12	0.12
Pre-tax Annual Profit[1] (£m/yr)	-72.5	-75.3	-87.1	-87.1	-102	-114
CT Payable over 20 years (£m)	795	820	831	831	866	941
IRR (%)	36	40	39	39	43	53
NPV (£m)	787	817	946	946	1106	1250
NPV (£/tonne)	71.3	74	86	86	100	113

Notes: [1]Calculated from Equation 6.16. The negative sign indicates that the project is in profit.

In this study, the hydrocracking scenario at 150 ktpa is revealed to be the most profitable one. However, governmental incentives to overcome corporation tax imposed on energy from waste (EfW) projects are lacking in the UK. Corporation tax on pyrolysis and hydrogenation is an obstacle that needs to be dealt with to encourage future investors to view plastics as a profitable feedstock. At scales exceeding 150 ktpa, both pyrolysis and hydrogenation proved to be profitable in this study. However, the corporation tax was a barrier that hindered the economic model performance for small scale (1 to 5 ktpa) TCT plants. In addition, there are no governmental incentives for heat production by pyrolysis (or gasification) in the UK. In fact, other than electricity produced by pyrolysis or gasification, no governmental incentives are granted to any TCT industry in the UK (see Band Table in Ofgem, 2011). Scenario 2 (MRF+IU+LTP) was determined to be the most environmentally friendly in terms of carbon savings (see Section 6.3.2). However, the results of this study point towards hydrogenation being more profitable at high economies of scale than incineration, dry materials recovery and pyrolysis.

6.5.1. Sensitivity Analysis

In this section, the effects of changing the input parameters on the economic performances of the different scenarios are evaluated. Fourteen different input parameters have been chosen for the sensitivity analysis and the effects of ±10% changes in these variables on the net present value (NPV) and internal rate of return (IRR) have been examined.

6.5.1.1. Effects of Changes in Input Parameters

Sensitivity analysis is a useful tool in evaluating the final calculated values of a techno-economic assessment. Sensitivity analysis takes into account the uncertainties in the input parameters, including increases or decreases in time dependant parameters, such as prices, efficiencies, etc. This can point to where the impacts of such parameters are most influential on the calculated profit. The results of the sensitivity analysis are presented in Tables 6.29-6.30, where the profit sensitivity is shown as the percent difference of the output with respect to its original value.

In Tables 6.29-6.30, the sensitivity analysis shows that the IU electrical efficiency, electricity selling price and waste calorific value have the greatest impact on the project total profit. In contrast, the capital cost (CC), PRN prices, and LEC prices had a negligible effect on the NPV and IRR.

Table 6.29 Sensitivity analysis results on the NPV performed on the three studied scenarios (±10% Change).

Scenario no.	1	2	3
Unit Operations	MRF+IU	MRF+IU+1ktpa LTP	MRF+IU+1ktpa VCC
Base Value (£/tonnes)	57.1	57.3	57.1
Input parameter	% Change	% Change	% Change
IU Elec. Eff +10%	16	16	16
IU Elec. Eff -10%	-16	-16	-16
IU Heat Eff +10%	8	8	8
IU Heat Eff -10%	-8	-8	-9
Capital Costs +10%	0	0	0
Capital Costs -10%	0	0	0
ROCs Price +10%	3	3	2
ROCs Price -10%	-3	-3	-3
LEC Price +10%	0	0	0
LEC Price -10%	0	-1	0
PRNs Price +10%	0	0	0
PRNs Price -10%	0	0	0
Elec. Price +10%	13	13	13
Elec. Price -10%	-13	-13	-13
Heat Price +10%	8	8	8
Heat Price -10%	-8	-8	-8
Discount Rate (i) +10%	-5	-5	-5
Discount Rate (i) -10%	5	5	5
IU OMC +10%	-3	-3	-3
IU OMC -10%	3	3	3
Tax Rate +10%	0	0	0
Tax Rate -10%	0	0	0
Collection Cost +10%	4	4	4
Collection Cost -10%	-4	-4	-4
Transportation Cost +10%	1	1	1
Transportation Cost -10%	-1	-1	-1
Calorific Value +10%	26	26	26
Calorific Value -10%	-21	-21	-21

Table 6.30 Sensitivity analysis results on the IRR performed on the three studied scenarios (±10% Change).

Scenario no.	1	2	3
Unit Operations	MRF+IU	MRF+IU+1ktpa LTP	MRF+IU+1ktpa VCC
Base Value (£/ tonnes)	33	33	33
Input parameter	% Change	% Change	% Change
IU Elec. Eff +10%	30	27	30
IU Elec. Eff -10%	-30	-30	-30
IU Heat Eff +10%	15	15	15
IU Heat Eff -10%	-15	-15	-15
Capital Costs +10%	-3	-3	-3
Capital Costs -10%	6	6	6
ROCs Price +10%	6	6	6
ROCs Price -10%	-3	-3	-3
LEC Price +10%	3	3	3
LEC Price -10%	0	0	0
PRNs Price +10%	0	0	0
PRNs Price -10%	0	0	0
Elec. Price +10%	24	24	24
Elec. Price -10%	-24	-24	-24
Heat Price +10%	15	15	15
Heat Price -10%	-15	-15	-15
Discount Rate (i) +10%	0	0	0
Discount Rate (i) -10%	0	0	0
IU OMC +10%	-9	-9	-9
IU OMC -10%	12	9	12
Tax Rate +10%	-24	-24	-24
Tax Rate -10%	30	30	30
Collection Cost +10%	-9	-12	-12
Collection Cost -10%	12	12	12
Transportation Cost +10%	0	0	0
Transportation Cost -10%	0	0	0
Calorific Value +10%	48	48	48
Calorific Value -10%	-42	-42	-42

6.5.1.2. Effects of Changes in Electrical Generation Efficiency

The electrical generation efficiency of the IU (mass-burn) was a very sensitive parameter to change, affecting in turn the NPV and IRR calculated in all three scenarios. This is demonstrated in this study when the scenarios' NPV and IRR increased by 16% and 30% with a 10% change, respectively. The incineration efficiency used in this study (η_{elec} = 18%) is a reasonable average value for combustion worldwide (Murphy and McKeogh, 2004). In the UK, this average efficiency for an IU is also acceptable for mass-burn processes and Murphy and McKeogh (2004) reported a similar average electrical generation efficiency in their study. In addition, a maximum of 22% was also reported for a similar unit in their study.

6.5.1.3. Effects of Changes in Heat Generation Efficiency

Heat generation efficiency proved to be a quite sensitive parameter. A high efficiency of 50% was used in this work, which is quite common in the CHP industry; hence in reality this value is unlikely to change.

6.5.1.4. Effects of Changes in Electricity and Heat Selling Prices and ROCs Prices

The price of electricity and heat (as utilities) is ever changing in the UK. Utilities companies are one of those responsible for this and play a major role in setting the prices. Revenue represented as NPV and IRR gained from electricity sales showed a ±13% and ± 24% change in the sensitivity analysis carried out (Tables 6.29-6.30). A change of ±8% and ±15% was obtained for the heat selling price. It is essential to keep the electricity and heat prices at a price equal to or higher than ones used in this study to ensure a profit from the three scenarios. The same argument could also be put forward for the ROC prices. The UK Government announced that suppliers of electricity will be entitled to ROCs until the 31st March 2037 (Patel et al., 2011).

6.5.1.5. Effects of Changes in IU OMC and Discount Rate

Running and operating costs are very hard to predict, as they are subject to labour, chemicals, suppliers, purchase and handling costs. In this analysis, the effect of changing the incineration unit's (IU) operating and maintenance cost (OMC) was assessed. The IU OMC proved to be a sensitive parameter when subjected to a ±10% change. A ±3% change in NPV and a ±12% change in IRR were witnessed. It is very important to keep the IU OMC (£40 per tonne) subjected to a minimal change to ensure the profitability of the project. Additionally, the discount rate has proven to be a sensitive parameter. All NPV calculated at a discount rate (i) of 6% were positive, showing a ±5% change (see Table 6.29). The discount rate was taken as 6% in this study as previously used for EFW UK projects by Patel et al. (2011). However, HM treasury recommends a 3.5% discount rate to be used in all public sector projects (Yassin et al., 2009). Hence, in this work higher risks associated with private investments are accounted for.

6.5.1.6. Effects of Changes in Waste Calorific Value

The sensitivity of the economic performance to change in the calorific value of waste is very important. This is especially true for the IRR which showed up to a ±48% change (see Table 6.30). Since unit performance is related to its input, waste with higher calorific value results in more energy recovery. This allows the IU to produce more electricity and heat to supply the needs of the market. Therefore, it is crucial that changes in waste composition are kept to a minimal. This is very difficult as waste composition is unlikely to remain stable, due to changing recycling rates, population habits and waste policies. Nonetheless, techno-economic studies should account for the changes in the waste calorific value during the plant's lifetime.

6.6 Conclusions

This chapter has reported the results of an attributional life cycle assessment (ALCA) performed on three scenarios that reflect plastics treatment in the greater London area (GLA). The polymeric fraction treated by the three integrated scenarios was part of the municipal solid waste (MSW) produced by the residents of the boroughs of Greenwich, Lewisham, Westminster, Bromley and the City of Exeter, Devon. At present, these boroughs send their MSW to an incineration unit (IU) with combined heat and power (CHP) and a dry materials recovery facility (MRF). This conventional processing of waste treatment was considered as the baseline scenario (scenario 1), and was compared with two other scenarios set within the same system boundaries. Scenarios 2 and 3 implement a pyrolysis reactor and a hydrogenation reactor to an extracted stream of the MRF plastics products, respectively.

Avoided burdens, through material recycling, incineration and thermo-chemical treatment (TCT), were included in the scenarios investigated as part of the system expansion methodology followed. These included the MRF products, electricity and heat produced from the incineration unit and gases, liquids, waxes and energy in the form of steam for the pyrolysis process. In addition, it included syncrude, gases and HCl from the hydrogenation unit. Average and marginal electricity production technologies were considered as avoided burdens for each investigated scenario and these technologies included the UK average electricity grid mix and four marginal electricity production processes (wind, nuclear, hard coal and natural gas). The UK marginal combined cycle gas turbine (CCGT) production mix was used to off-set the heat produced by each scenario.

In terms of global warming potential (GWP), the marginal hard coal treatment technology showed the highest GWP savings for all studied combinations for the three scenarios. This is due to the fact that the hard coal off-setting conversion factor was the highest of all the avoided

electricity treatment options, resulting in larger carbon savings. All the combinations studied for the three scenarios were negative, which indicates that all the treatments considered credited the system studied. Scenario 2 showed the largest carbon savings in comparison to the other two scenarios. This is due to larger amount of products produced by the low temperature pyrolysis (LTP) process, which contributes to the total avoided burdens of this scenario. An increase of 1.2×10^7 kg $CO_{2\text{-eq}}$ (compared to scenario 1) and 9×10^6 kg $CO_{2\text{-eq}}$ (compared to scenario 3) of GWP savings are achieved per year due to the implementation of the pyrolysis process. This indicates that pyrolysis is more preferable than PSW incineration and hydrogenation in terms of carbon savings.

Economically, hydrogenation is the most favourable option for waste treatment (including the polymeric fraction) at the scale of 150 ktpa for the VCC unit. Additionally, it gave the highest net present value (NPV, £113 per tonne) and internal rate of return (IRR, 53%) compared to scenario 1 (NPV of £57 per tonne and an IRR of 33%) and scenario 2 at a scale of 150 ktpa for the LTP unit which resulted in a NPV of £43 per tonne and IRR of 43%. However, the corporation tax (CT) is highest in scenarios with hydrocracking. This is due to the higher pre-tax profits and CC of scenario 3 (hydrocracking) compared to scenarios 1 and 2 (pyrolysis) over the scenario's lifetime. A 96% increase in pre-tax annual profit (TP) is calculated for the 150 ktpa VCC unit addition to the base scenario (MRF+IU). Furthermore, a 19% increase in corporation tax is also reported for the addition of the 150 ktpa VCC unit due to higher profits. The addition of the LTP unit was also profitable at scales exceeding 50 ktpa. However, the profitability from VCC sales exceeded the ones generated from the LTP process due to product sales and prices.

Finally, both TCT technologies implemented in this study (scenario 2 and 3) to treat plastics have proven to be more environmentally friendly and economical than incineration (scenario 1). In particular, pyrolysis has shown greater carbon savings than incineration and hydrocracking. However, governmental incentives to overcome corporation tax imposed on energy from waste (EfW) projects are lacking in the UK. Corporation tax on pyrolysis and hydrogenation is a serious obstacle that needs to be dealt with in order to encourage future investors to view plastics as a profitable feedstock. If such policies were to be proposed in the future, EfW technologies would be considered as both green and profitable technologies that could be developed in the UK.

Chapter 7

Conclusions and Future Work

Polymers are the most versatile material of the modern age and are the basic building block of what we know as plastics. Polymers are a crude oil derivative, the result of oil refineries and the conversion of petrochemicals, including ethylene, propylene, styrene, benzene, etc. Polymers have a very high calorific value compared to other crude oil products, (such as kerosene, gas and heavy oil, etc) and other municipal waste fractions (such as organics, textiles and plastic solid waste mixtures). The UK has committed to a new target of 50% reduction of greenhouse gases (GHGs) by 2025 compared to the 1990 levels and currently 80% of the UK carbon emission is the result of fossil fuels burning. Consequently, the development of low carbon technologies and efficient waste management treatments are crucial. These technologies include thermolysis and treatments of a chemical nature of solid waste produced by the different activities of our urban environment.

The main objective of this work was to investigate the thermo-chemical treatment (TCT) of polymers at different scales. The research investigated TCTs ranging from laboratory scale processes to industrial scale units. The different products yielded by laboratory and industrial scale TCT units were assessed and in addition, the formation mechanism of such products was also evaluated in a laboratory scale pyrolysis process. The contribution that such technologies make to our urban environment was addressed through a life cycle assessment (LCA) approach.

Within this framework, the thesis began with a comprehensive review providing an insight into the different types of chemical treatments and TCT at different scales of operation and in addition, the different types of products recovered from each industrial unit were assessed. The review also included a detailed illustration of the reaction mechanisms used to describe the products formed by pyrolysis. This was undertaken because the experimental and kinetics modelling work undertaken in this thesis was on the pyrolysis process.

At the laboratory scale, the pyrolysis of five polyolefins under isothermal conditions was studied in a thermogravimetric analyser using data provided by Ravago Plastics (Belgium) for polyolefins and end of life tyres (ELTs). This was performed to determine the polymers

degressive behaviour, as well as the chemicals yielded by this process and led to the development of a novel approach to model the depolymerisation of polyolefin reactions based on lumped products. The depolymerisation model included primary, secondary and tertiary reactions that contribute to the different products formed by pyrolysis. The model enabled the kinetic assessment of the pyrolysis reaction and resulted in an overall activation energy that was in agreement with previous findings reported in the literature. The same method was applied to analyse the results from the isothermal pyrolysis of end of life tyres (ELTs), and a model was proposed based on an isothermal experiment performed at 500°C to determine the products yielded by the reaction.

This thesis assessed the effect of implementing TCT reactors, such as pyrolysers, on the urban environment by performing an attributional life cycle assessment (ALCA) as part of the waste management treatment strategy of London. A life cycle assessment (LCA) accounts for every stage in the cycle of a product or process, from resource extraction (cradle) to the ultimate end-of-life treatment (grave). Reports showed that material recycling emits the lowest volatile organic compounds when compared to incineration and landfilling. Improving polymers recovery (namely PE) has been reported by Tarantini et al. (2009) to reduce environmental indicators. Incineration with energy recovery in combined heat and power (CHP) plants are environmentally preferable when the electricity produced is off-set against electricity produced from coal. A limited number of reports on the technical and economic data for industrial scale TCT technologies are available in the literature (Tukker et al., 1999, Holighaus et al., 1994; Perguini et al., 2005). In fact, a comparative assessment of such technologies against conventional methods has never been undertaken in the UK and this is considered a gap in the recent research activities that warrants further investigation.

The ALCA was conducted on three scenarios that reflect the management of waste in the greater London area (GLA). All scenarios included a materials recovery facility (MRF), an incineration unit (IU) with combined heat and power (CHP), and transfer stations (TSs) for waste segregation. The MRF represents the Greenwich MRF station which was visited in December 2009. The purpose of the visit was to gain knowledge of the different operations undertaken within the station that can contribute to the overall energy and environmental burdens as well as the economic aspects investigated. The IU (with combined heat and power, CHP) incorporated in this work represents the South East London Combined Heat and Power (SELCHP) station located in Lewisham (London). A baseline scenario (scenario 1) was defined to reflect the current route of treatment in the GLA and this included a MRF and IU. Scenarios 2 and 3 implemented a BP low temperature pyrolysis (LTP) unit and a VCC hydrogenation unit, respectively. The feeds for both industrial scale TCT units were taken as 1000 tpa of the plastics extracted from the MRF recovered products. The scenarios studied treat plastics produced from

the following locations:

1. Borough of Greenwich
2. Borough of Lewisham
3. Borough of Bromley
4. Borough of Westminster
5. City of Exeter (Devon)

Finally, the techno-economic performance of these scenarios was evaluated. The net present value (NPV) and internal rate of return (IRR) for each scenario was determined and the most profitable routes of treatment were identified. The total costs included capital costs (CC) and operating and maintenance costs (OMC) together with revenues obtained including governmental incentives such as renewable obligation certificates (ROCs), levy exemption certificates (LECs) and packaging recovery notes (PRNs).

7.1. Main Conclusions

The main conclusions of this thesis are summarised below:

- A novel kinetic model based on lumped products was proposed in this work for the pyrolysis of polyolefins and end of life tyres (ELTs) tested. This lumped product approach has not been attempted in the past for pyrolysis reaction kinetics. Results were in agreement with previous findings validating the developed mechanism and approach.

- Pyrolysis also showed the largest carbon savings in comparison to hydrogenation and materials incineration. This is due to the large amount of products produced by pyrolysis, which contributes to the total avoided burdens and credits for the system studied.

- From an economic point of view, hydrogenation is the most favourable option as it results in the highest net present value (NPV) and internal rate of return (IRR) compared to pyrolysis and incineration. This is mainly due to the revenue hydrogenation generates from the sales of its products (syncrude, naphtha, etc.) and gate fees.

- The sensitivity analysis revealed that the waste calorific value, electrical and heat generation efficiencies of the IU are the most sensitive parameters which greatly affect the economic performance of polymers pyrolysis, hydrogenation and incineration.

7.2. Key Highlights Extracted From the Thesis

The main highlights from the thesis are summarised below:

- A model that can be applied to all polyolefins tested was proposed that involved the primary reaction of depolymerisation of the polymer material to an intermediate stage (waxes), a secondary reaction that produced gases, liquids and aromatics, and finally, the tertiary reaction which contributes to the liquid fraction from the gases formed. The lumped product approach proposed in this work was not performed in the past on pyrolysis degradation mechanisms. The reaction order (n) of polymer depolymerisation ranged between 0.97-0.1, and the overall kinetic rate constant (k_o) ranged between 0.37×10^{-2} to 0.29 s^{-1} for the various grades of PE studied, which is in agreement with previous reports by various authors (Ceamanos et al., 2002; Dahiya et al., 2008). The overall activation energy ranged between 211 – 230 kJ mol^{-1}, which fell within the range of previous findings for PE pyrolysis (see Figure 3.39). A similar approach has not been undertaken in the past on pyrolysis kinetics modelling. This approach eases the development of future models for pyrolysis reactions and can lead to a simple relationship being applicable in industry that can determine the products yielded at different temperatures for different polymers.

- Specific patterns were observed during the pyrolysis experiments of the polymers tested. Waxes (> C_5) always resulted in the highest estimated fraction of the final products assessed (44 to 69%). This is in agreement with previous findings by Aznar et al. (2006) and Zia et al. (2007), which showed that tars (including waxes) form the largest fraction of the pyrolysis products on average (45%). The melting point of the virgin grades (HDPE and LDPE) had a direct impact on their wax formation and it was noted that the lower the melting point the quicker the wax formed as the reaction progressed.

- The model proposed was able to determine the polymers fractions at different reaction times, which were compared to the experimental results obtained. HDPE no.1 demonstrated an almost an identical match between the experimental and model results for the first 50 s of the reaction at 500°C. Observing the pattern for the two HDPE grades, it was noted that HDPE no.2 had a smaller margin of error between the experimental and model results for the 500°C experiment. Results for 550°C and 600°C were all within a ±10% margin of error. At 550°C the values plotted were scattered within a ±10% deviation, which covered the error for the LDPE. This behaviour is very similar to that exhibited by HDPE no.1, MDPE no.1 and no.2 polymers at 550°C. It was observed that based on the mechanism proposed, the higher the operating temperatures the higher the error of the model prediction versus experimental values.

- A thermal cracking scheme was proposed for the end of life tyres (ELTs) grade studied based on the global yielded products, which were lumped into four categories, namely gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char. Evaluation of the depolymerisation kinetics (from primary, secondary and tertiary reactions) showed a high match with the experimental results, resulting in an overall rate constant (k_o) of 0.011 (s^{-1}). Results from this case study showed the potential for this kinetics modelling approach to be carried out in the future. Previous reports have focused solely on maximising gas yield; however, the products yielded by the isothermal pyrolysis experiments showed a very promising result, with gases and char (marketed as carbon black) constituting 60% of the total products formed. However, more data points are necessary in order to thoroughly validate the work presented here for ELTs. This will aid in the development of a general model that could help develop a kinetics relationship applicable in industry.

- Attributional life cycle assessment (ALCA) was conducted on three scenarios that reflect the management of waste in the greater London area (GLA). The energy turnover for all three scenarios is negative, indicating that the energy output is larger than the energy input, which credits all the scenarios in this study. The energy turnover was of the same order of magnitude in all scenarios studied, although the energy outputs in scenarios 2 and 3 are dependent on their plastics throughput as feed. This strengthens the argument for diverting more plastics towards pyrolysis and hydrogenation in order to produce more EfW in London.

- The global warming potential (GWP) is used for each scenario to analyse the carbon savings. The attributional life cycle assessment (ALCA) in this study is combined with system expansion, which enables the assessment of the avoided burdens from the processes included in the system studied. Different electricity production technologies were assigned to combination numbers. These technologies included the average UK electricity mix, marginal hard coal, marginal nuclear, marginal wind and marginal natural gas. All the combinations studied are negative, which indicates that all the treatments considered credit the scenario studied. Furthermore, combination 5 (avoided burden resulting from electricity produced from marginal hard coal technology) shows the optimal treatment of all combinations studied in scenarios 1, 2 and 3. This is due to the fact that the hard coal off-setting conversion factor was the highest of all the avoided electricity treatment options.

- Scenario 2 shows the largest carbon savings in comparison to the other two scenarios studied. This is due to larger amount of products produced by the LTP process, which contributes to the total avoided burdens of this scenario. By comparing the most

environmentally friendly combination (combination 10, pyrolysis with electricity produced from hard coal) to combinations 5 and 15 (baseline and hydrogenation with electricity produced from hard coal, respectively), 1.2×10^7 kg $CO_{2\text{-eq}}$ (compared to scenario 1) and 9×10^6 kg $CO_{2\text{-eq}}$ (compared to scenario 3) of GWP savings are achieved per year due to the implementation of the pyrolysis process. This indicates that pyrolysis is more preferable than PSW incineration and hydrogenation in terms of carbon savings.

- The economic viability of the overall system was investigated. The three scenarios investigated include a dry materials recovery facility (MRF), incineration unit (IU) combined with a heat and power (CHP) plant, low temperature pyrolysis (LTP) plant and a VCC hydrogenation plant. The addition of a 1 ktpa unit of both TCT units (i.e. LTP and VCC) to the overall system was investigated accommodating the maximum available amount of plastics in the scenarios. Moreover, the addition of a 50, 100 and 150 ktpa units of LTP and VCC was investigated to assess the overall economic viability of the developed system with scales high enough to compete with the MRF and IU.

- Economically, hydrogenation is the most favourable option for waste treatment (including the polymeric fraction) at the scale of 150 ktpa for the VCC unit. Additionally, it gave the highest net present value (NPV, £113 per tonne) and internal rate of return (IRR, 53%) compared to scenario 1 (NPV of £57 per tonne and an IRR of 33%) and scenario 2 at a scale of 150 ktpa for the LTP unit which resulted in a NPV of £43 per tonne and IRR of 43%.

- Furthermore, the corporation tax (CT) is highest in scenarios with hydrocracking. This is due to the higher pre-tax profits and CC of scenario 3 (hydrocracking) compared to scenarios 1 and 2 (pyrolysis) over the scenario's lifetime. A 96% increase in pre-tax annual profit (TP) is calculated for the 150 ktpa VCC unit addition to the base scenario (MRF+IU). Moreover, a 19% increase in corporation tax is also reported for the addition of the 150 ktpa VCC unit due to higher profits.

- The addition of the LTP unit was also profitable at scales exceeding 50 ktpa. However, the profitability from the VCC hydrocracking unit sales exceeded the ones generated from the LTP process due to higher pre-tax profits generated from product sales.

- A sensitivity analysis was performed on the three scenarios' input parameters to test their effect on the project's total cost. This revealed that the waste calorific value, electrical and heat generation efficiencies of the IU are a very sensitive parameter which greatly affects the economic performance of the scenario.

In conclusion, this thesis addressed the performance of thermo-chemical treatment (TCT) units at industrial and laboratory scales, as well as their impact on the urban environment. The thesis also highlights the feasibility of integrating TCT as part of the waste management strategy for plastic solid waste (PSW). Pyrolysis proved to be a very promising process that can successfully produce highly desirable petrochemicals and energy from polymers. It was shown that on a small scale (laboratory) it has the potential to produce large fractions of waxes, gases and liquids that could be comparable in calorific value to petrochemicals and refinery cuts such as naphtha, butane and pentane, however their use in the UK is still very limited. With the exception of the Compact Power Plant in Avonmouth (near Bristol) which treats MSW, organics and medical waste via pyrolysis, there are no other serious industrial efforts utilising pyrolysis currently being undertaken in the UK. However, at large scales (150 ktpa) hydrogenation has proven to be an economical option that can compete with incineration and dry materials recovery in the UK. It is estimated that plastics recovery in the UK is lower than that of Germany by 50% (PE, 2007). The pyrolysis process has proven to be an environmentally friendly option which with energy production could be integrated into existing waste treatments infrastructures. With the right level of incentives and the political will, the work undertaken in this thesis demonstrated that TCT, particularly pyrolysis, is a promising technology for the improvement of waste management strategies and the reduction of the carbon footprint of plastics.

7.3. Future Work and Recommendations

This thesis has considered thermo-chemical treatment (TCT) of polymers at different scales by testing polymers in a micro laboratory scale pyrolysis process and implementing TCT industrial units to an urban environment (London). Future work could be to establish more environmentally friendly and energy efficient systems in the future. The recommendations given below are to be considered by an ascending order of priority.

As a next step, it would be useful to test more polymers in pyrolysis, gasification, hydrogenation and combustion laboratory experiments in an isothermal set-up to gain a more detailed comparison between the differences in product yields resulting from these processes against the same polymers tested in this work. Such work would complement the kinetics modelling undertaken here and could result in a more generic model being employed for these TCT processes that describes the depolymerisation mechanism of these reactions. More synthetic grade and pure laboratory preparations of polymers should be also tested and compared with the results obtained here. This could lead to understanding the differences

between the products formed by thermo-chemically treating commercial grades, pure polymers and recyclate grades recovered from different industrial processes (in-house recycling, containers, bottles, etc). In addition, it would be useful to up-scale these processes to a pilot plant process to gain a better understanding (if any) between the kinetic modelling conducted on laboratory micro scales and pilot plant ones. The kinetic model proposed in this work would benefit from pilot plant experiments to verify the approach and account for any differences in products obtained.

The isothermal pyrolysis of end of life tyres (ELTs) would benefit by experimenting with a large spectrum of tyre grades from a number of sources, in order to establish a database that can help develop further the tyre pyrolysis industry in this country. More experiments on ELTs would lead to a wider understanding of their depolymerisation mechanisms. In addition, the kinetics modelling approach developed in this thesis could be implemented for more polymer filled (rich) feedstock, such as polymer composites. This would lead to generalising the kinetics modelling approach undertaken in this work and would accommodate a larger range of polymers. Performing pilot scale experiments may also lead to a deeper understanding of the effect of scale.

In Chapter 6, the study focused on the greater London area (GLA) by developing the scenarios for boroughs that are located in the proximity of central and suburban London. The life cycle assessment (LCA) conducted in this thesis can be expanded in a number of ways. Firstly, more boroughs could be incorporated in the analysis to expand the boundaries of the study. These boroughs could be included with respect to other MRFs in London in order to incorporate more processing lines in the scenarios studied. This will also reflect a more realistic scenario for the additional plastic materials needed to develop 150 ktpa scale TCT plants. Secondly, hotspot analysis (HSA) could be performed to understand which step in the IU, MRF, LTP and VCC processes contribute the most to the environmental burden emissions. To achieve this, an industrial partner in this field would be highly desirable. Thirdly, more TCT reactor data could be utilised to expand the work carried out in this thesis. TCT units such as the Pyromelt process, Texaco gasification and blast furnace application units have all been successful in the past. A close industrial relationship could benefit the work carried out here in implementing TCT units in London and other urban communities, by securing data not available within the available literature. It will also lead to understanding the changes on products recovered from different TCT units resulting from the kinetics model developed. This will result to a more in-depth study of the impact of the kinetic parameters estimated on the environmental and economical performance of the TCT units studied.

The CHP plant considered in this study was assumed to have 100% market penetration. In

other words, the electricity and heat are always assumed to be sold to distributing companies regardless of their current demands. This warrants an investigation in the long run into district heating and power distribution to local communities, as well as the cost and technologies of storing energy in such units. This could lead to a detailed comparison with different scenarios that the LCA work presented in this thesis can build on.

Electricity production off-setting data used in this thesis reflected the UK average and marginal data. However, it would be more desirable to see whether further GWP savings could be achieved when electricity production is considered as a marginal hydro process or production for district heating. Can such technologies compete against off-setting the electricity produced from hard coal marginal data? This point leads to investigating more heat production off-setting methods (e.g. steam turbines), and comparing them against the CCGT marginal production conversion factor used in this work.

The crude oil industry has benefited immensely from the development of TCT reactors. This is due to the fact that most TCT reactors use similar technologies to those already existing in oil refineries and petrochemical complexes (e.g. steam and catalytic cracking). Performing an environmental and economical assessment study on the prospects of integrating existing crude oil processing complexes and TCT reactors is definitely a highly desirable research prospect in the future. This would show whether TCT units could decrease the carbon footprint of refineries and petrochemical complexes. It would also provide an economical foundation for increasing the feedstock of a refinery (by adding a PSW throughput) and gaining a higher profit margin that contributes to the existing refinery production line. In addition, the quality issue of TCT units could be addressed and solved simultaneously. The products generated from the TCT units could be mixed with products from oil processing complexes to improve the quality of them (if needed) or be marketed separately. This economic assessment could help to improve the economic performance of such oil complexes and improve the economic performance of TCT processes.

Finally, in order to find the optimal economy of scale for the LCA system studied in Chapter 6, a multi-objective optimisation framework could be formulated. Solving the superstructure resulting from integrating the carbon savings and techno-economic performance of the system studied would yield trade off solutions. These would point towards the optimal scale for all the units considered (MRF, IU, VCC and LTP), as well as the optimal environmental and economical solution.

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List of Abbreviations

AET;	Aquatic Ecotoxicity
ALCA;	Attributional Life Cycle Assessment
AR;	Atmospheric Residue
ASR;	Automobile Shredded Residue
BFB;	Bubbling Fluidized Bed
CERT;	UK Carbon Emission Reduction Target
CFB;	Circulating Fluidized Bed
CHP;	Combined Heat & Power
CLCA;	Consequential Life Cycle Assessment
DAR;	Depletion of Abiotic Resources
EA (UK);	Environmental Agency (in the United Kingdom)
EfW;	Energy from Waste
ELT;	End of Life Tyres
FBR;	Fluidized Bed Reactor
FID;	Flame Ionization Detector
FT;	Fourier Transform
GC;	Gas Chromatography
GHGs;	Greenhouse Gases
GLA;	Greater London Area
GMRF;	Greenwich Materials Recovery Facility
GRT;	Gas Residence Time
H/C;	Hydrogen to Carbon
HAT;	Human Air Toxicity
HC;	Hydrocarbons
HST;	Human Soil Toxicity
HT;	Human Toxicity
HWT;	Human Water Toxicity
IPCC;	International Panel on Climate Change
IPPC;	Integrated Pollution Prevention and Control
IR;	Infrared
ISO;	International Standardization Organization
ISW;	Industrial Solid Waste
IU;	Incineration Unit
IWM;	Integrated Waste Management
KSF;	Kinetic Severity Function

LCA; Life Cycle Assessment
LCI; Life Cycle Inventory
LCIA; Life Cycle Impact Assessment
LCPD; Life Cycle Product/Process Design
LP; Linear Programming
LTP; Low Temperature Pyrolysis
LTs; Light Transformers
MILP; Mixed Integer Linear Programming
MINLP; Mixed-Integer Non-Linear Programming
MO; Multi-Objective
MRF; Materials Recovery Facility
MS; Mass Spectrometry
MSW; Municipal Solid Waste
NAFTA; North America Free Trade Agreement
NTR; Number of Trips Required
OF; Objective Function
PAHs; Polycyclic Aromatic Hydrocarbons
PC; Petrochemical
POF; Photochemical Oxidant Formation
PRNs; Packaging Recovery Notes
PSW; Plastic Solid Waste
RCEP; Royal Commission on Environmental Pollution
RDF; Refuse Derived Fuel
RK; Runga-Kutta
rxn; Reaction
SBR; Styrene Butadiene Rubber
SRT; Solid Residence Time
TCD; Thermal Conductivity Detector
TCT; Thermo-Chemical Treatment
TET; Terrestrial Ecotoxicity
TGA; Thermogravimetric Analysis
THC; Total Hydrocarbons
TOC; Total Organic Carbons
TS; Transfer Station
UV; Ultra Violet
WDA; Writing-Down Allowance

Polymer Abbreviated Names

ABS; Poly (Acrylonitrile, Butadiene, Styrene)

EPS; Expanded Polystryene

EVA; Ethylene Vinyl Acetate

HDPE; High Density Polyethylene

IPP; Isotactic Polypropylene

LDPE; Low Density Polyethylene

LLDPE; Linear Low Density Polyethylene

MDPE; Medium Density Polyethylene

PCA; Polycarbonate

PE; Polyethylene

PET; Polyethylene Terephthalate

PI; Polyisoprene

PLA; Polylactide

PMMA; Poly (methyl methacrylate)

PP; Polypropylene

PS; Polystyrene

PVA; Polyvinyl Alcohol

PVC; Polyvinyl Chloride

List of Symbols

a; Degree of polymerization of the largest molecule that can be vaporized

A_i; Tars formed in reaction i.

AP; Acidification Potential (kg SO_2-eq)

A_P; Primary tars

B_i; Emission (kg) of Substance i.

C_{CH4}; Amount of Carbon in Methane Emitted from Landfill (Gg/annum).

C_i^n; Benchmark Concentration (mol/m^3) for Chemical i.

CSR_i^{nm}; Concentration (mol/m^3) of chemical i to source ratio in medium m (soil, water, etc) based on a unit release (mol/m^3) to compartment n (air, water, etc.).

DOC ; Degradable Organic Carbon Generation (Gg/annum)

E_a; Apparent activation energy (kJ mol^{-1})

ec_i; The AP of Substance i Expressed Relative to the Value for SO_2

e_i; Emission (kg) of Substance i.

$Emission_{Corr}$; Corresponding emission of substance i (tonne).

$ETP_i^{air,m}$; Emission to air.

ETP_i^{nm};	Ecotoxicity Potential Expressing Release of Chemical i to Compartment n in Terms of Equivalent Quantities of Chemical i Released to the Same Compartment.
$ETP_i^{sw,m}$;	Emission to Surface Water (sw).
$f(\alpha)$;	Function that represent the rxn model
FA^*;	Standard Measure of Harm, e.g. fraction of species adversely affected
$G_{i;}$	Gases formed in reaction i.
G_P;	Primary gases
GWI;	Global Warming Index
GWP;	Global Warming Potential (kg CO_2-eq)
GWP_i;	Global Warming Potential of Substance i
IBA;	Incinerator Bottom Ash
ICR_i^m;	Impact to Concentration Ratio for Chemical i in Environmental Medium m
m_o;	Initial charge of polymer (gm)
M_o;	Initial mass of the sample
MSW_T;	Total Municipal Solid Waste Produced by a System
N;	Number of TG data points
n;	Reaction order
ODI_i;	Ozone Depleting Index
ODP_i;	Ozone Depleting Potential of Substance i
O_n;	Alkene in Ranzi et al. (1997) model
OT;	Operating Temperature
P,	Polymer (Radical Chain Mechanism)
PE;	Amount of polyethylene present at any time, $PE = P + P^*$.
PEC_i^n;	Predicted Environmental Concentration (mol/m^3) of Chemical i in Medium m
P_n;	Polymer in Ranzi et al. (1997) model
Q_{CH4};	Annual CH_4 Emission from Landfill (Gg/annum).
RDF;	Refuse Derived Fuel
R_p;	Primary radical (Radical Chain Mechanism)
R_s,	Stable radical (Radical Chain Mechanism)
S;	Surface exposed to the surrounding atmosphere (m^2)
S_i^n;	Continuous Release in (mol/day) to Compartment n
TCT;	Thermo-Chemical Treatment
$TE_{i,cCorr}$;	Corresponding Total Emission of Substance i,.
T_m;	Melting temperature (^oC)
T_{max};	Peak temperature (K)
W(t);	Mass of the polymer in the reactor at time (t) in gm (Horvat and Ng ,1999)

W_o; Initial mass of the polymer (gm)

x_i; Weight fraction of component i

$X_{w;}$ Amount of Waste Feedstock for Generating 1 tonne of Product Gas

Greek Letters

ζ; wt% Conversion = $(m_o - m)/m$)

α; Degree of polymer conversion = $(m_o - m)/(m_o - m_\infty)$

β; Heating rate ($^oC\ min^{-1}$)

Subscripts

1; Primary reaction in the scheme (wax formation)

2; Secondary reaction in the scheme (gas formation)

3; Secondary reaction in the scheme (liquid formation)

4; Secondary reaction in the scheme (aromatic formation)

5; Tertiary reaction in the scheme (liquid to gases)

a; Aromatics

f; Final

∞; Final state (e.g. last recorded temperature)

g; Gases

l; Liquids

p; Polymer

w; Waxes

Appendix A

Theoretical Fit and Model Results as a function of reaction time (s)

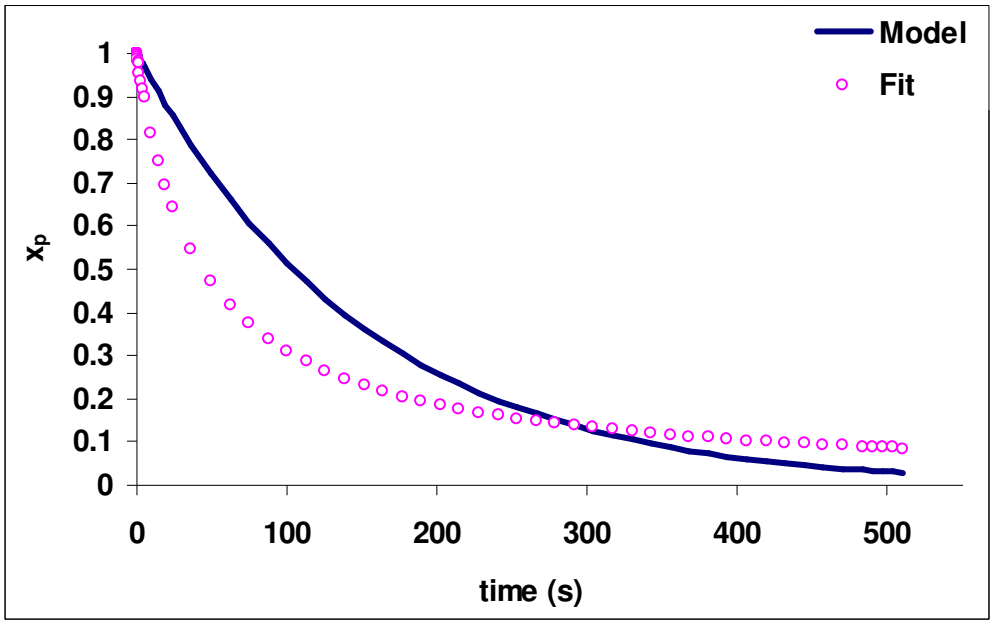

Figure A.1 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.1 at 500ºC with a regression coefficient (R^2) of 0.97.

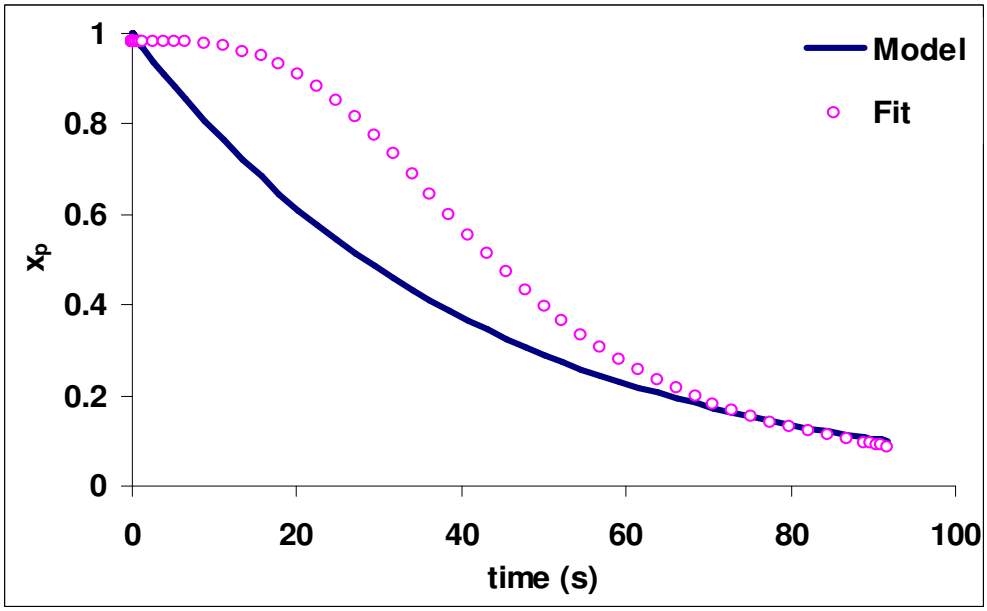

Figure A.2 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.1 at 550ºC with a regression coefficient (R^2) of 0.95.

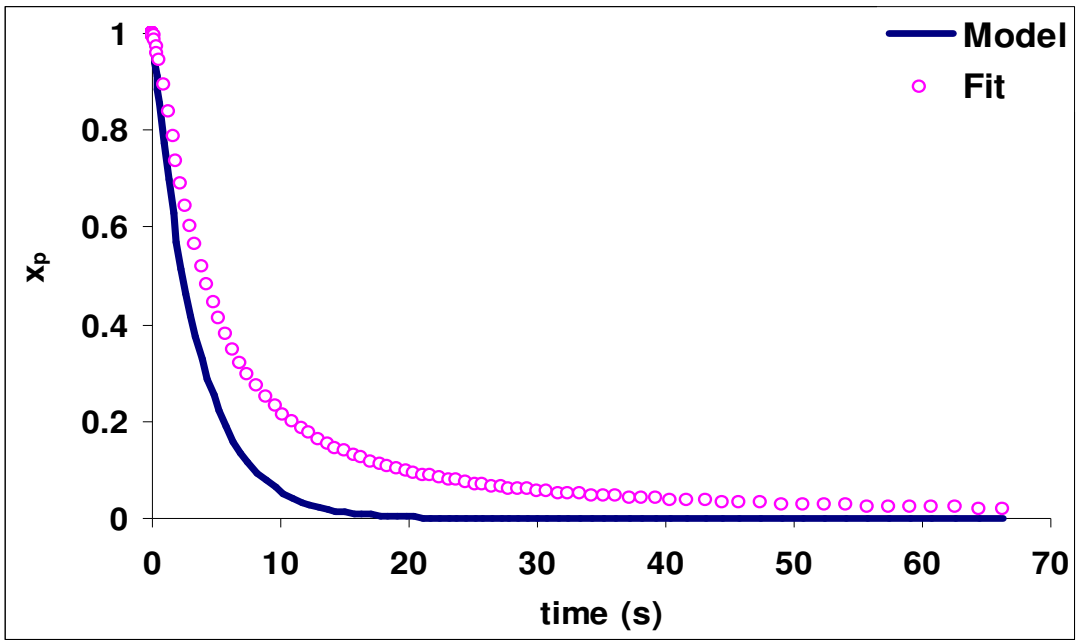

Figure A.3 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.1 at 600ºC with a regression coefficient (R^2) of 0.98.

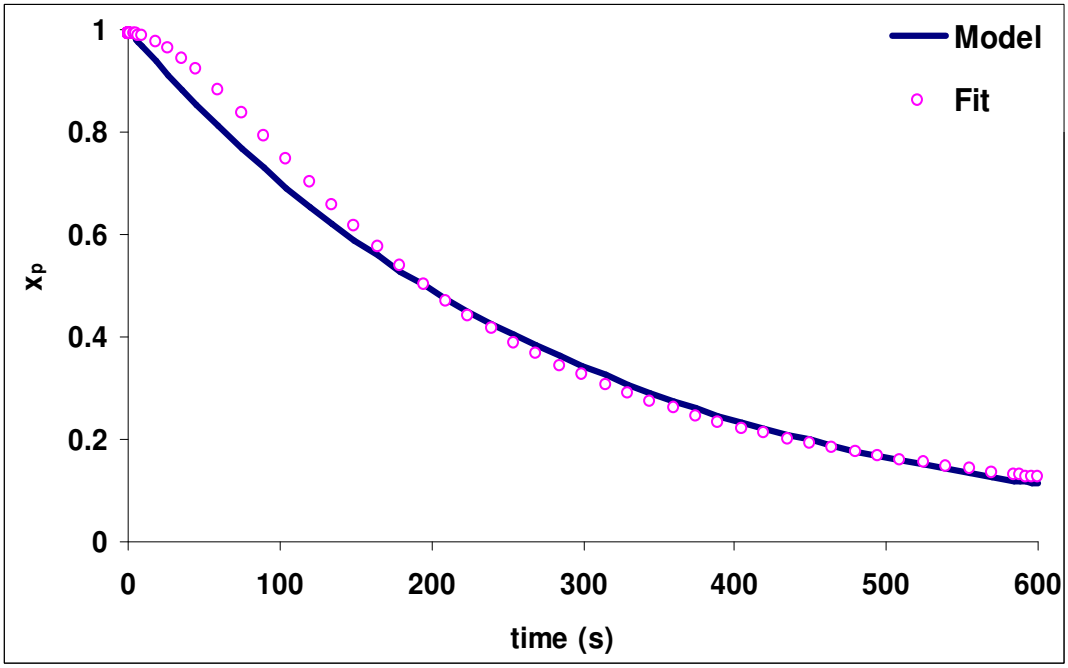

Figure A.4 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.2 at 500ºC with a regression coefficient (R^2) of 0.99.

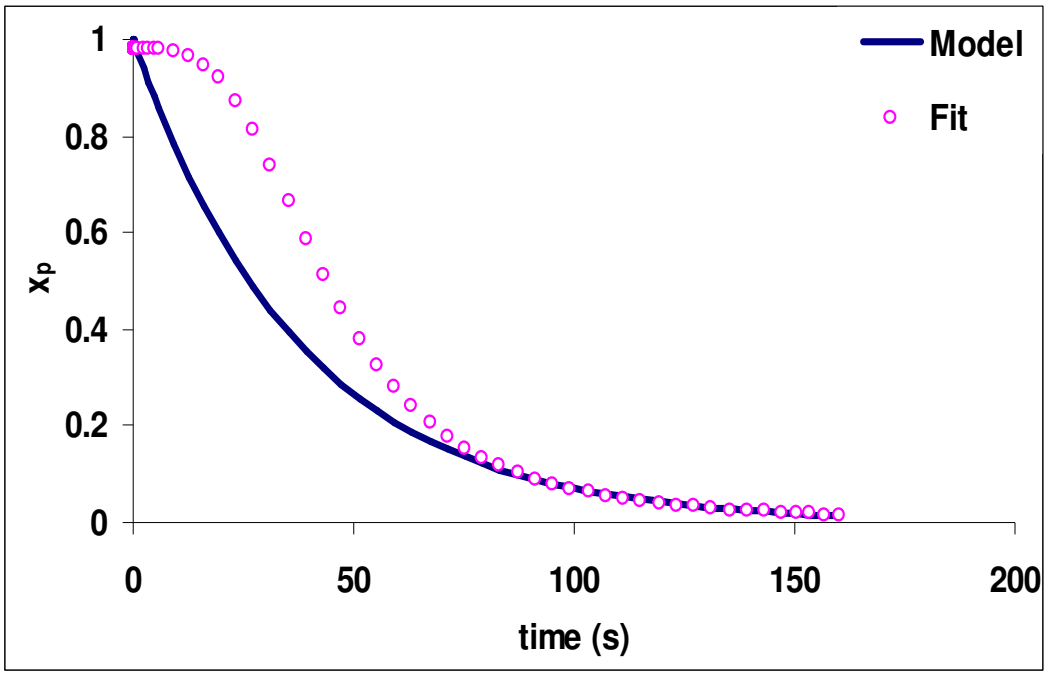

Figure A.5 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.2 at 550ºC with a regression coefficient (R^2) of 0.97.

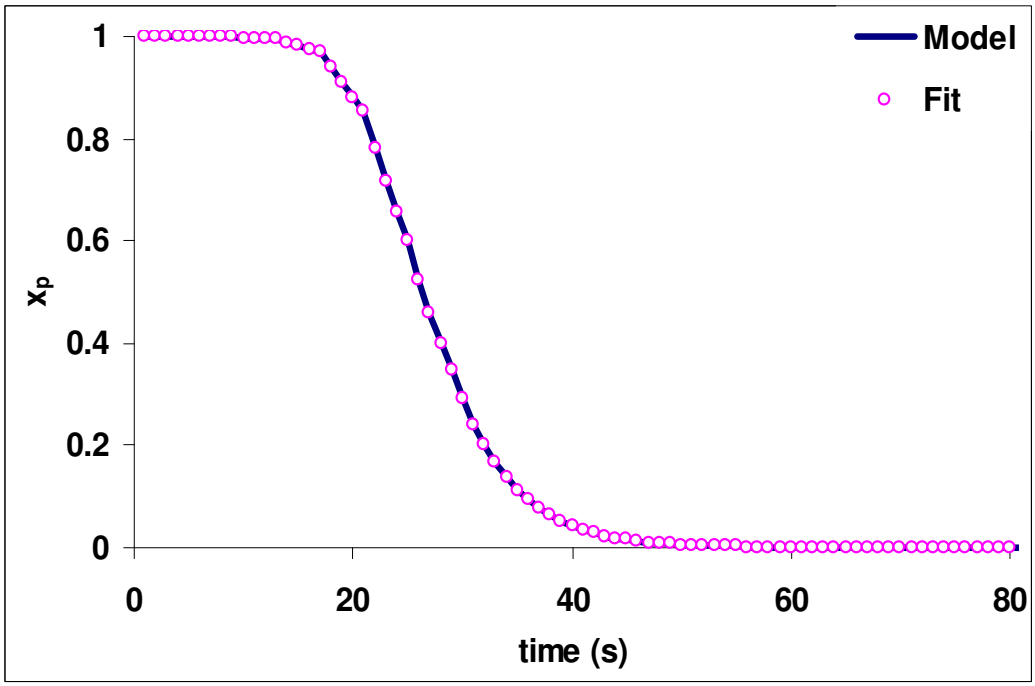

Figure A.6 – Theoretical fit and model results of polymer fraction (x_p) for HDPE no.2 at 600ºC with a regression coefficient (R^2) of 0.99.

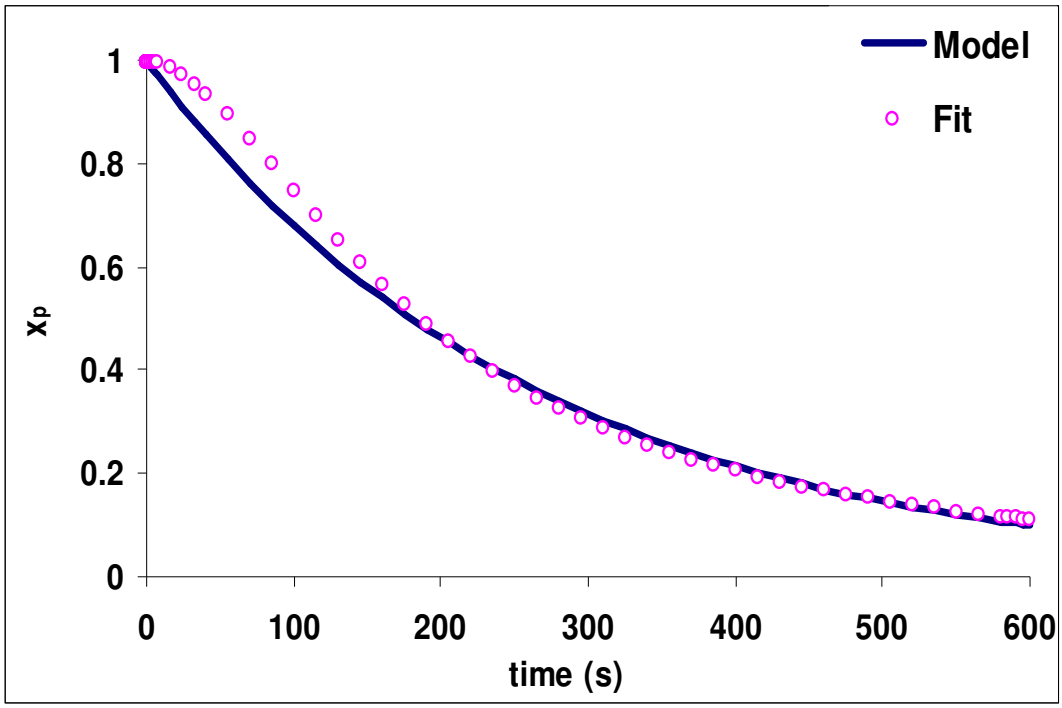

Figure A.7 – Theoretical fit and model results of polymer fraction (x_p) for LDPE at 500ºC with a regression coefficient (R^2) of 0.99.

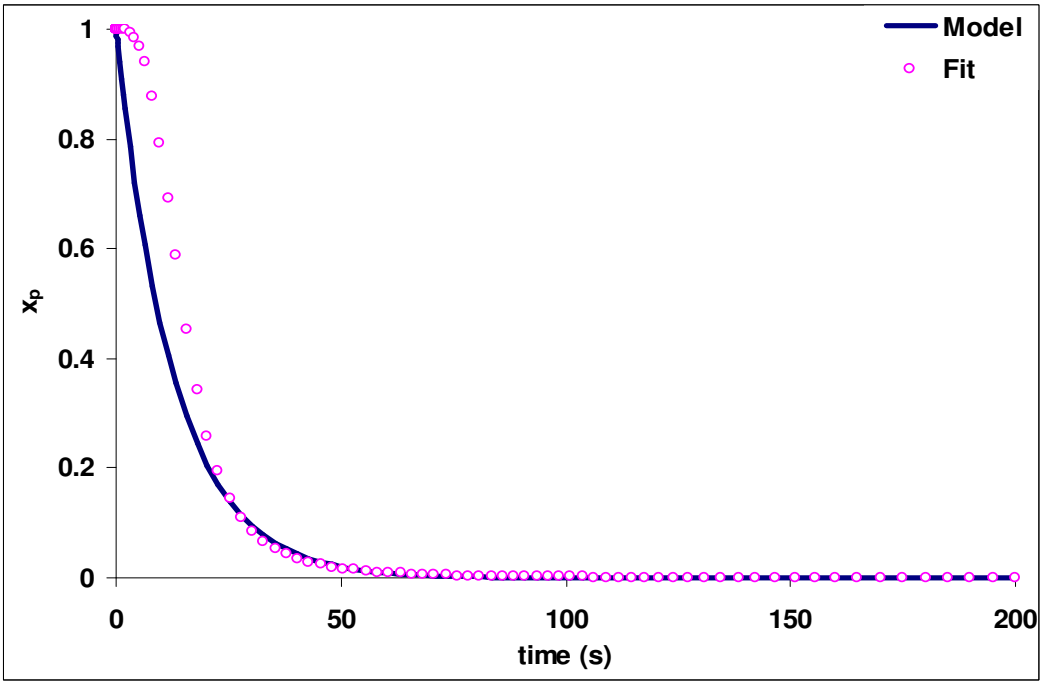

Figure A.8 – Theoretical fit and model results of polymer fraction (x_p) for LDPE at 550ºC with a regression coefficient (R^2) of 0.98.

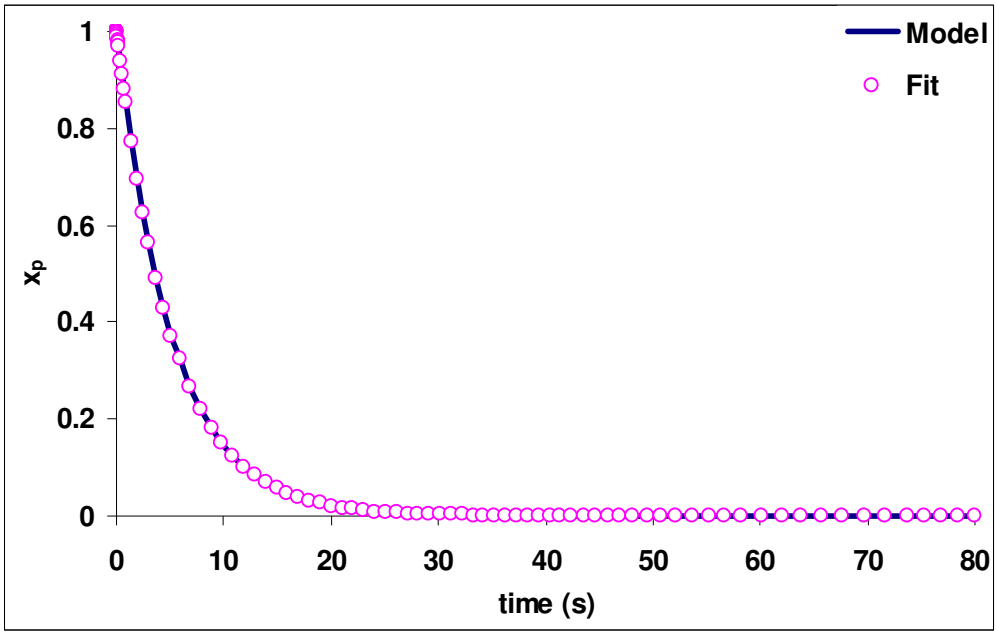

Figure A.9 – Theoretical fit and model results of polymer fraction (x_p) for LDPE at 600ºC with a regression coefficient (R^2) of 0.99.

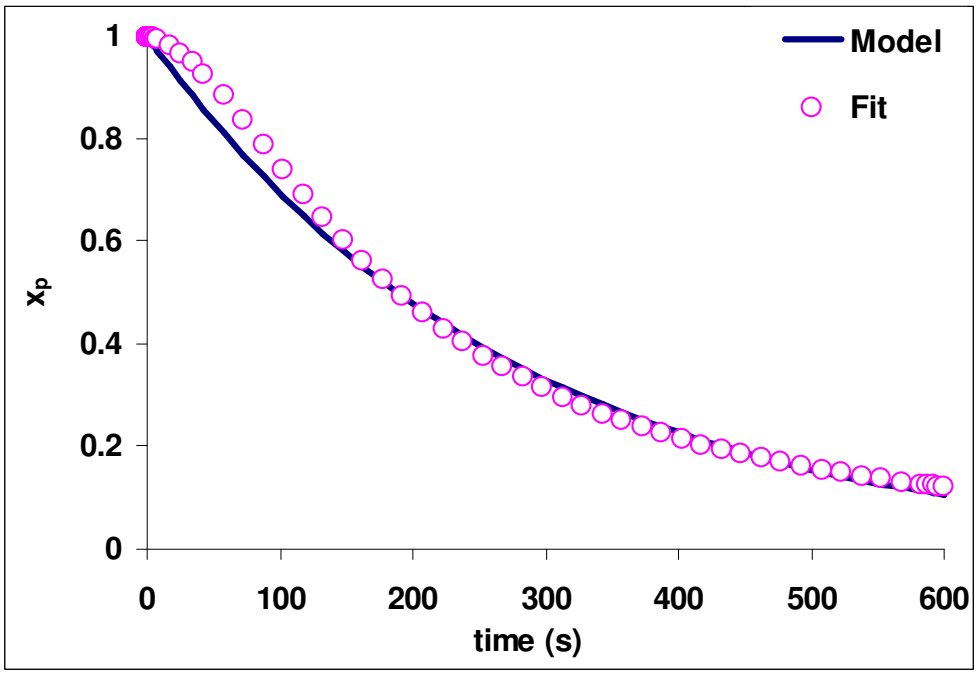

Figure A.10 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.1 at 500ºC with a regression coefficient (R^2) of 0.99.

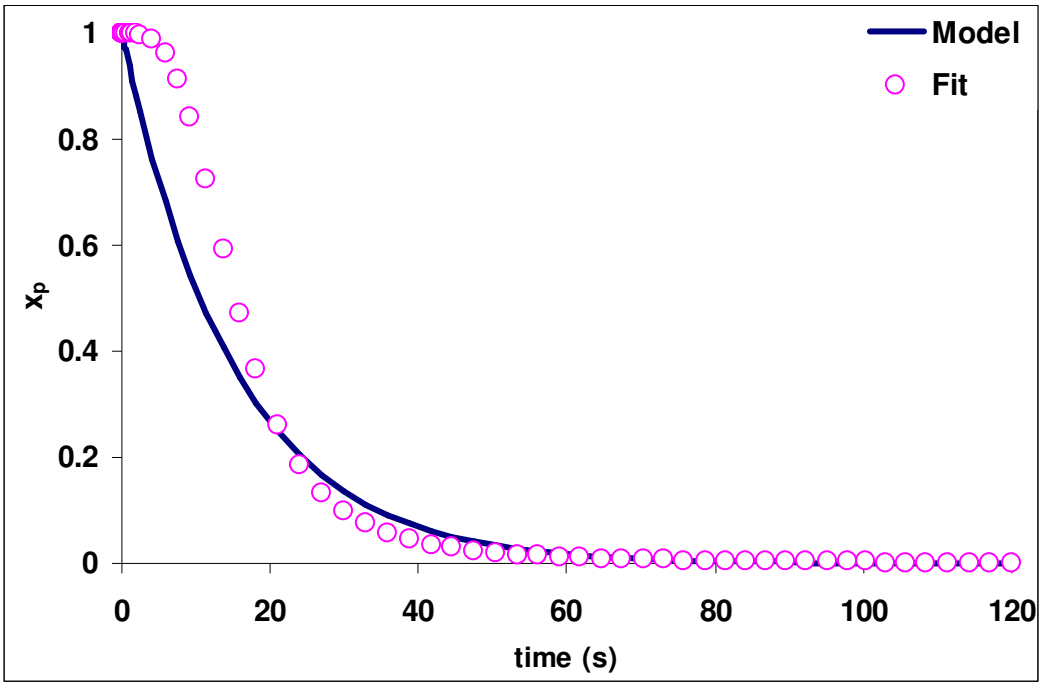

Figure A.11 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.1 at 500ºC with a regression coefficient (R^2) of 0.98.

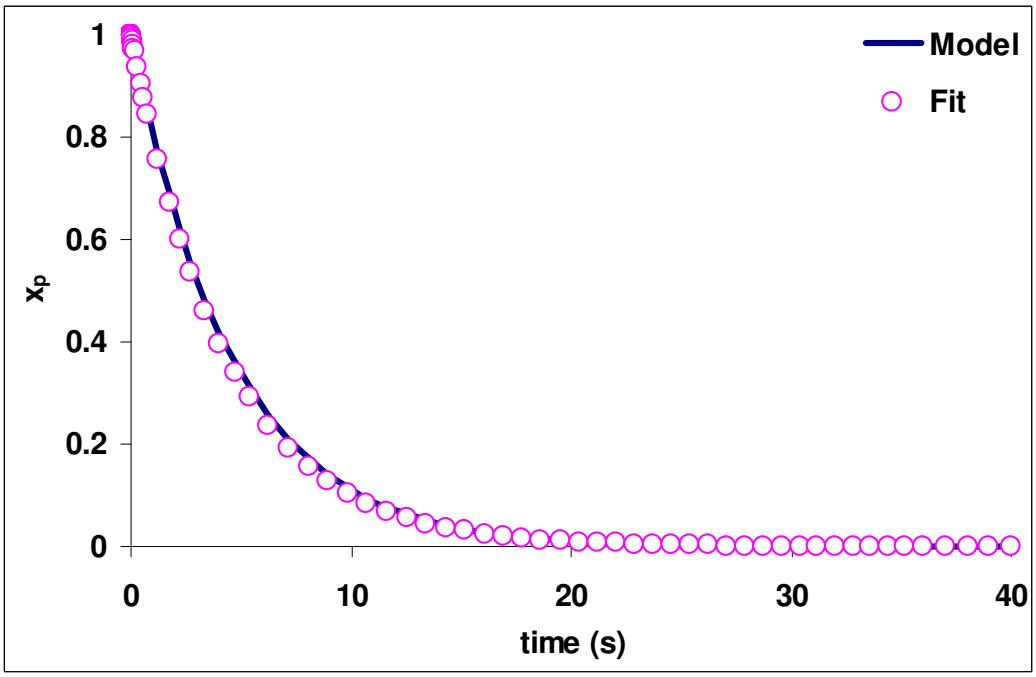

Figure A.12 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.1 at 600ºC with a regression coefficient (R^2) of 0.99.

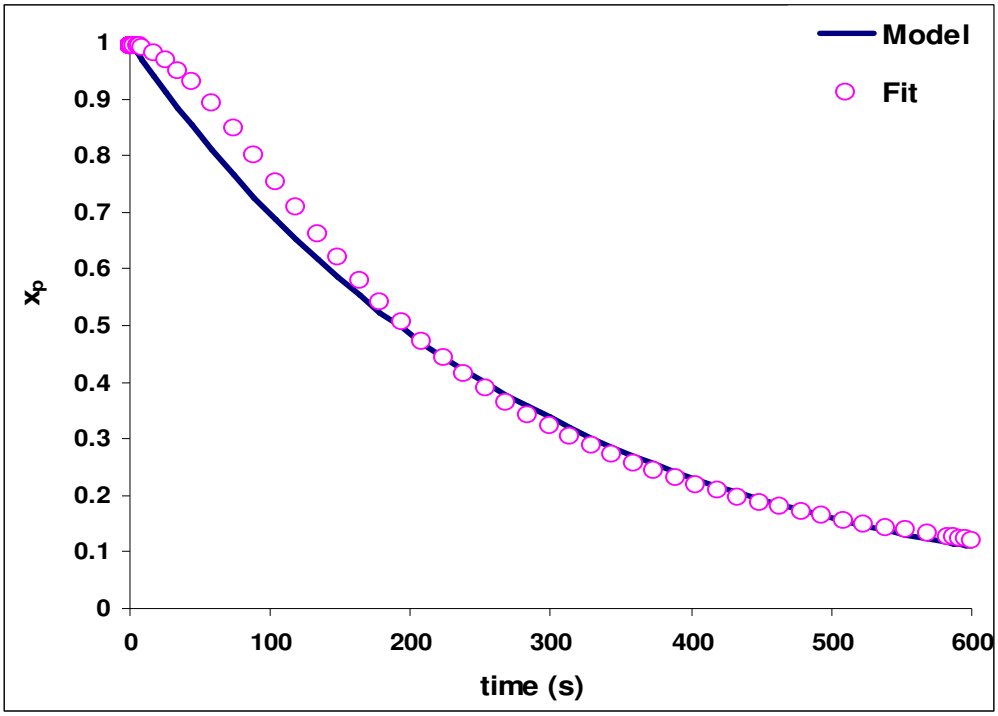

Figure A.13 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.2 at 500ºC with a regression coefficient (R^2) of 0.99.

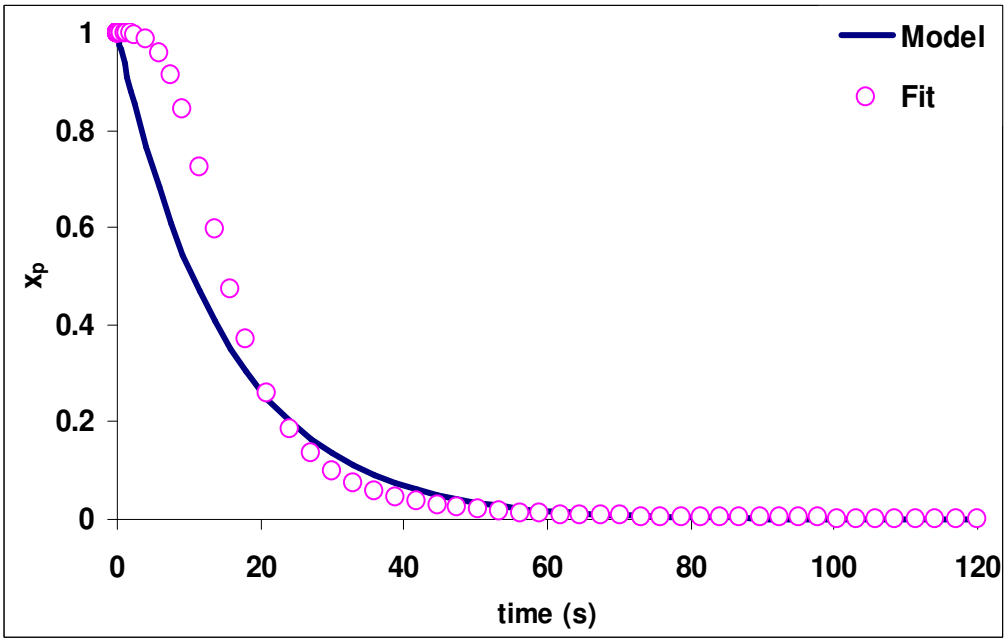

Figure A.14 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.2 at 550ºC with a regression coefficient (R^2) of 0.98.

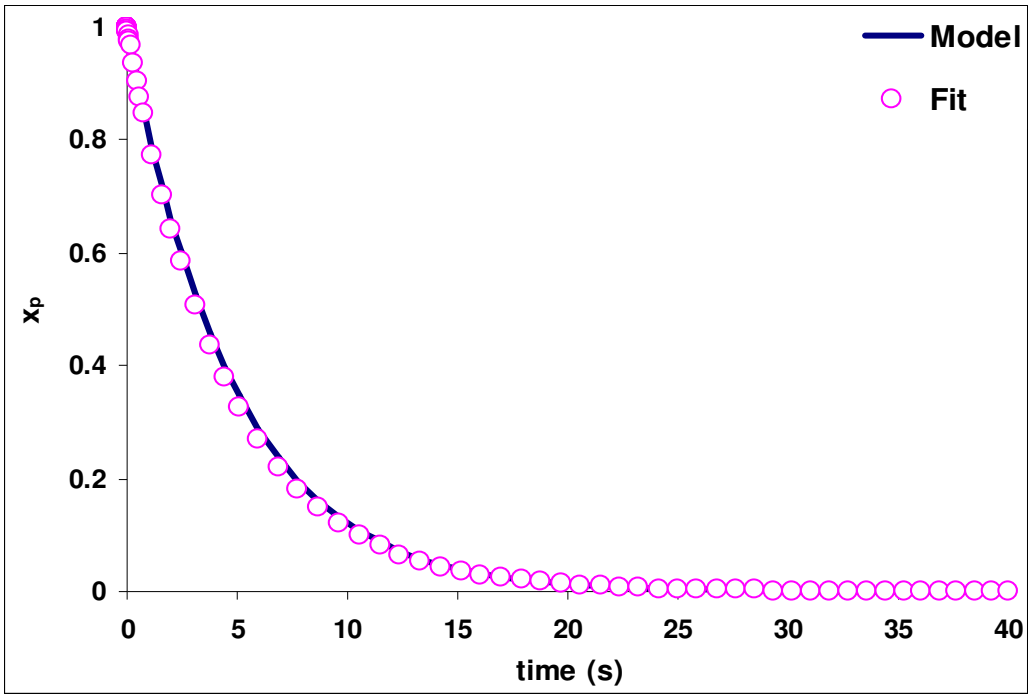

Figure A.15 – Theoretical fit and model results of polymer fraction (x_p) for MDPE no.2 at 600ºC with a regression coefficient (R^2) of 0.99.

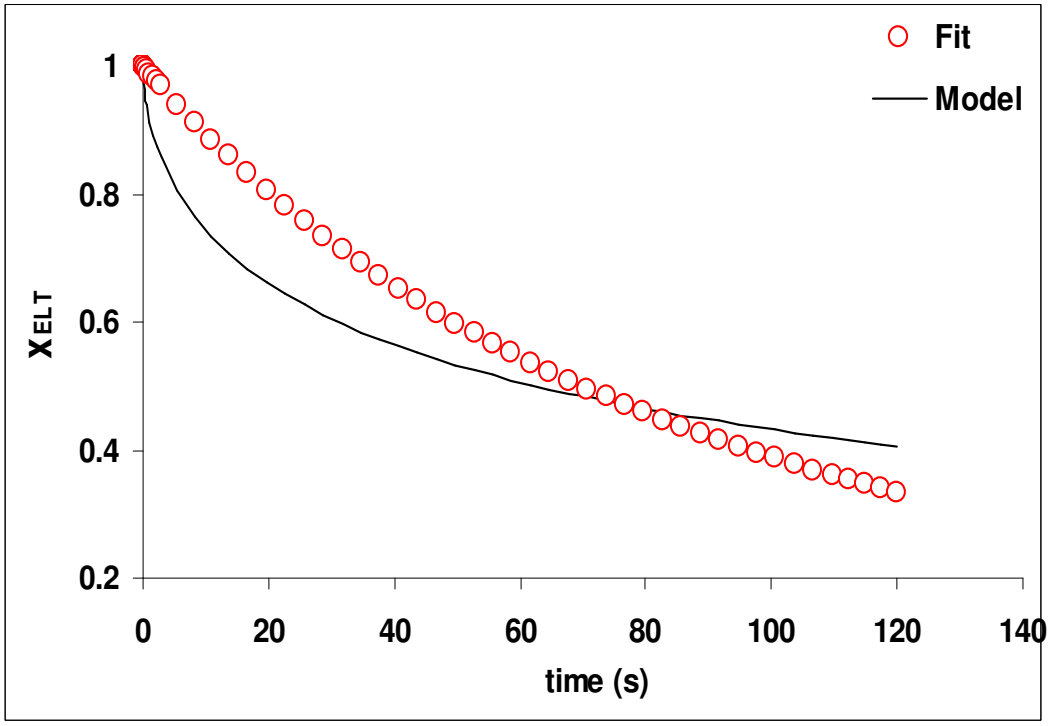

Figure A.16 – Theoretical fit and model results of End of life tyres fraction (x_{ELT}) with a regression coefficient (R^2) of 0.96.

Appendix B

Theoretical Fits used for the Runge-Kutta Solution in the Matlab to Represent the Experimental Polymer Weight Loss

Table B.1. Data fit equation* parameters used to represent the experimental polymer fraction (x_p) in solving the 4th order Runge-Kutta system in the case of HDPE no.1, showing %Sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)	a	b	c	d	%SE	R^2
500	510	4.32	4.32	0.11	0.97	106.07	0.97
550	91.7	5.5	5.67	3.22×10^{-5}	3.24	98.09	0.98
600	66.3	3.85	3.85	0.54	1.4	371.8	0.99

* The data fit equation used was the following: $x_p = \frac{a}{b + c(t)^d}$; where x_p is the polymer fraction and t is the time (s).

Table B.2. Data fit equation* parameters used to represent the experimental polymer fraction (x_p) in solving the 4th order Runge-Kutta system in the case of HDPE no.2, showing %Sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)**	a	b	c	d	%SE	R^2
500	600	29.50	29.75	0.003	1.74	93.60	0.99
550	160	0.04	-	-	-	850.65	0.99
600	80	0.14	-	-	-	103.19	0.99

* The data fit equation used was the following (at 500°C): $x_p = a \big/ b + c(t)^d$; where x_p is the polymer fraction. At both temperatures of 550 and 600°C, the following exponential fit was used: $x_p = \exp(-at)$.

** To avoid dividing by zero, at 550°C; x_p was taken as 0.001 and at 600 °C it was taken as 0.0001.

Table B.3. Data fit equation* parameters used to represent the experimental polymer fraction (x_p) in solving the 4th order Runge-Kutta system in the case of LDPE, showing %Sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)**	a	b	c	d	%SE	R^2
500	600	32.95	33.05	0.003	1.78	109.81	0.99
550	160	7.35	7.35	0.001	3.32	364.84	0.99
600	80	0.19	-	-	-	195.55	0.99

*The data fit equation used was the following (at 500 and 550°C): $x_p = a \big/ b + c(t)^d$; where x_p is the polymer fraction. At 600°C, the following exponential fit was used: $x_p = \exp(-at)$.

** To avoid dividing by zero, at 550 and 600°C the x_p value was taken as 0.0001.

Table B.4. Data fit equation* parameters used to represent the experimental polymer fraction (x_p) in solving the 4th order Runge-Kutta system in the case of grade no.1 of the recycled MDPE, showing %Sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)**	a	b	c	d	%SE	R^2
500	600	32.94	33.06	0.004	1.72	73.88	0.99
550	120	7.35	7.35	0.0009	3.32	218.40	0.96
600	40	0.23	-	-	-	123.45	0.99

*The data fit equation used was the following (at 500 and 550°C): $x_p = a / b + c(t)^d$; where x_p is the polymer fraction. At 600°C, the following exponential fit was used: $x_p = \exp(-at)$.

** To avoid dividing by zero, at 550°C x_p was taken as 0.001 and at 600°C it was taken as 0.0001.

Table B.5. Data fit equation* parameters used to represent the experimental polymer fraction (x_p) in solving the 4th order Runge-Kutta system in the case of grade no.2 of the recycled MDPE, showing %Sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)**	a	b	c	d	%SE	R^2
500	600	34.41	34.58	0.003	1.77	97.95	0.99
550	120	7.35	7.35	0.0009	3.32	216.51	0.96
600	40	0.23	-	-	-	119.59	0.99

* The data fit equation used was the following (at 500 and 550°C): $x_p = a / b + c(t)^d$; where x_p is the polymer fraction. At 600°C, the following exponential fit was used: $x_p = \exp(-at)$.

** To avoid dividing by zero, at 550°C x_p was taken as 0.001 and at 600°C it was taken as 0.0001.

Table B.6. Data fit equation* parameters used in solving the 4th order Runge-Kutta system in the case of Belgian grade ELT, showing % sum of error (%SE) and the regression coefficients (R^2) between experimental and calculated data points.

T (°C)	Reaction time (s)	a	b	c	d	%SE	R^2
500	120	0.22	0.22	0.02	0.58	71.32	0.96

* The data fit equation used was the following: $x_{ELT} = \frac{a}{b + c(t)^d}$; where x_{ELT} is the ELT fraction.

Appendix C

Gabi Extracted Models for Incineration Processes and Landfills

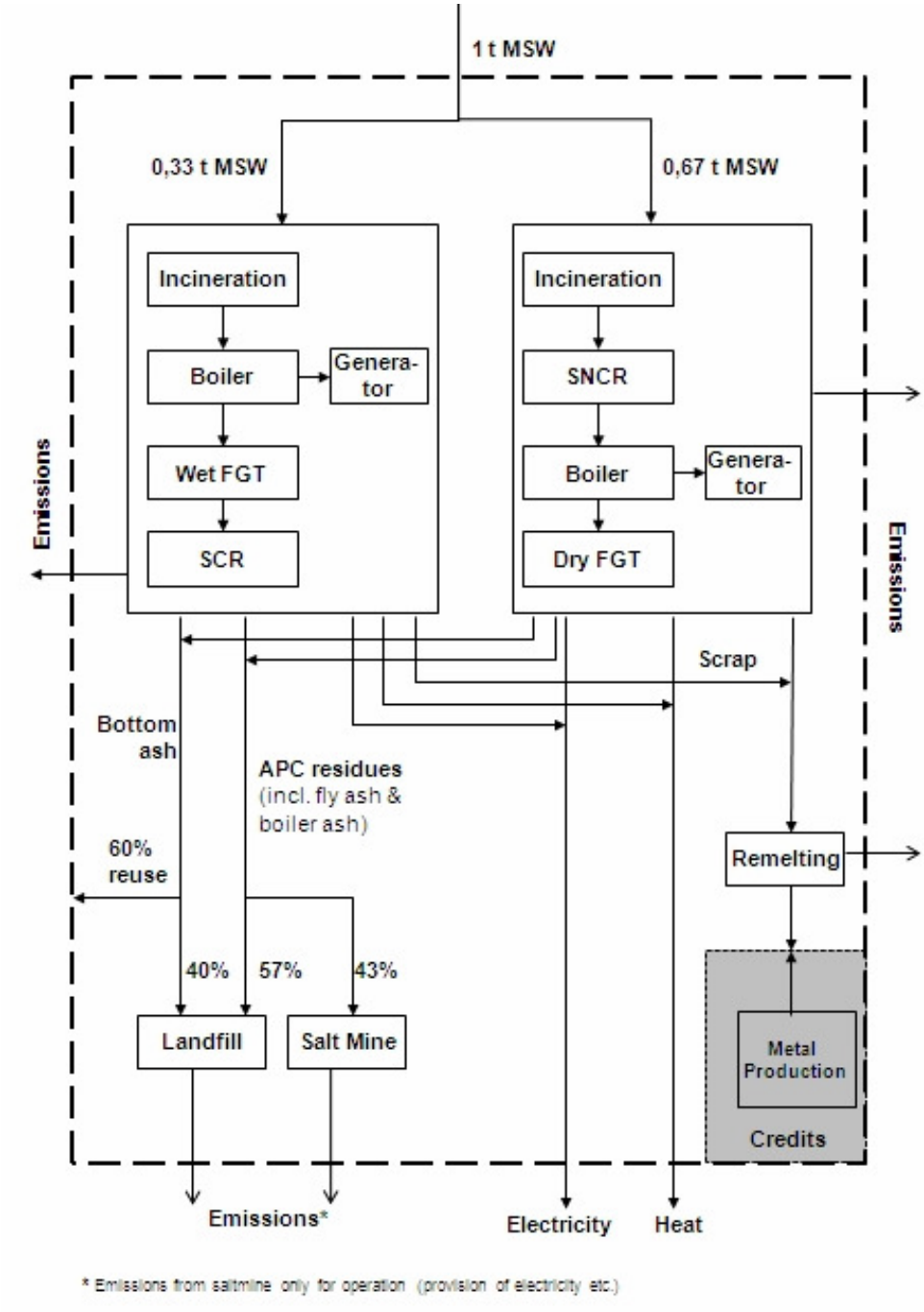

Figure B.1 - Gabi Incineration Model.

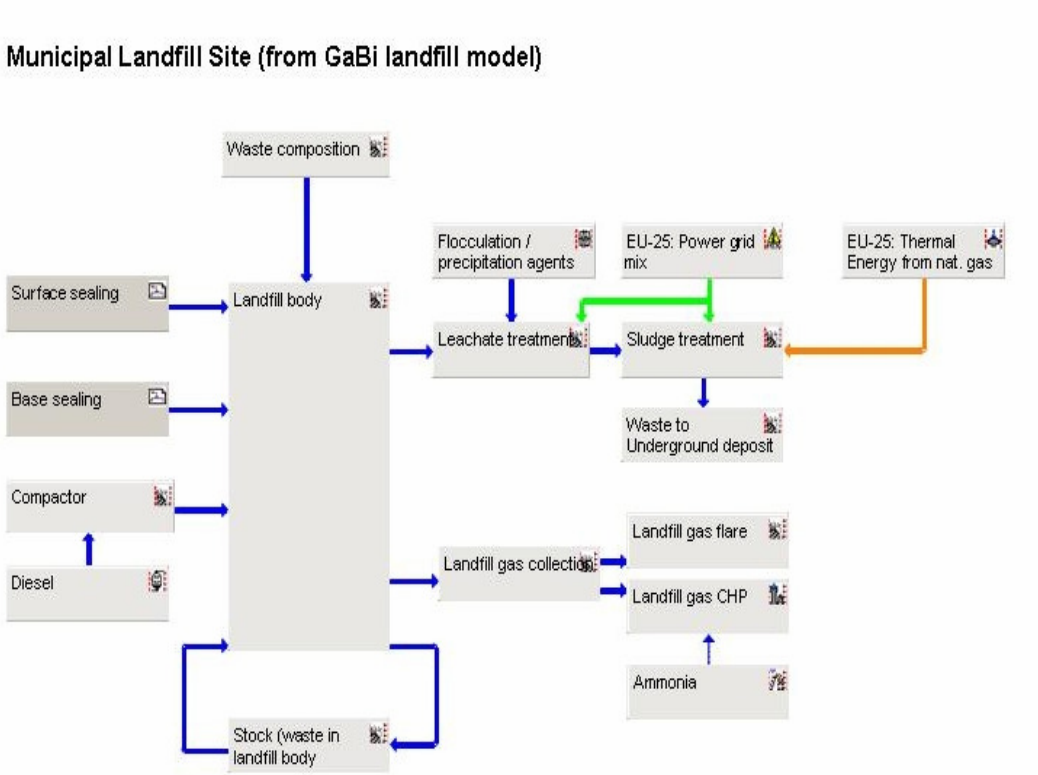

Figure B.2 - Gabi Landfill (EfW) Model. The data used in this work for comparison with landfilling considers this landfill model extracted from Gabi software.

Publications Extracted from This Work

Book Chapters:

1. Al-Salem, S.M. and Lettieri, P., (**2010**).
On the Pyrolysis of Polymers as a Petrochemical Feedstock Recovery Route, Chapter 12 in 'Chemistry and Chemical Engineering Research Progress', Edited by: A.K. Haghi, Nova Science Publishers, ISBN: 978-1-61668-503-4.

2. Lettieri, P. and **Al-Salem, S.M.**, (**2011**).
Thermo-Chemical Treatment of Plastic Solid Waste, Chapter 17 in 'Handbook of Waste Management and Recycling', Edited by: Trevor Letcher; Daniel Vallero, Elsevier, ISBN: 978-0-12381-475-3.

Refereed Journal Papers: *(Reverse Chronological Order)*

1. Al-Salem, S.M., Mechleri, E., Papageorgiou, L.G. and Lettieri, P. (**2012**).
Life cycle assessment and optimization on the production of petrochemicals and energy from polymers for the Greater London Area, *Computer Aided Chemical Engineering,* **30(1)**, 101-106.
Also In: Proc of the 22nd European Symposium on Computer Aided Process Engineering (ESCAPE 22), Part A; Edited by: Bogle, D., Fairweather, M., pp. 101-106, Elsevier.
Published also as a special edition of.
London (*England*), UK, 17th-20th June.

2. Al-Salem, S.M. and Lettieri, P., (**2010**).
Kinetic study of high density polyethylene (HDPE) pyrolysis, *Chemical Engineering Research & Design*, **88(12)**; 1599-1606.

3. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**).
The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, *Progress in Energy & Combustion Science*, **36(1)**: 103-129.

4. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**).
Kinetics and product distribution of end of life tyres (ELTs) pyrolysis: A novel approach in *polyisoprene* and *SBR* thermal cracking, *Journal of Hazardous Materials*, **172(2-3)**: 1690-1694.

5. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**).
Recycling and recovery routes of plastic solid waste (PSW): A review, *Waste Management*, **29(10)**: 2625-2643.

Refereed Conference Papers & Refereed Conference Posters:

1. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2008**).
Waste to energy solutions from polymeric based solid waste in the context of Life Cycle Assessment (LCA), In: Proc 2nd Energy Materials at UCL-Centre for Material Research Forum Meeting, pp. 19.
London (*England*), UK, 3rd December.

2. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**).
Thermal pyrolysis of High Density Polyethylene (HDPE), In: Proc 9th European Gasification Conference: Clean energy and chemicals,
Düsseldorf, Germany, 23rd-25th March.

3. Al-Salem, S.M. and Lettieri, P., (**2009**).
Output analysis of using mathematical modelling (IWM-2 Model) for Municipal Solid Waste Management (MSWM) in the state of Kuwait: A Life Cycle Inventory (LCI) of polymeric based waste, In: Proc 2nd Kuwait Waste Management Conference & Exhibition,
Kuwait City, State of Kuwait, 14th-16th April.

4. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**).
Thermal cracking kinetics of high density polyethylene (HDPE) particles via dynamic thermogravimetry in an inert atmosphere**,** In: Proc 10th UK Particle Technology Forum,
Birmingham (*England*), UK, 1st-2nd July.

5. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2009**).
Thermal treatment of different grades and types of polyethylene (PE) wasted articles**,** In: Proc 8th World Congress of Chemical Engineering (8th WCCE), Paper ID# 1734, pp. 1-4.
Montreal (*Quebec*), Canada, 23rd-27th August.

6. Al-Salem, S.M., Lettieri, P. and Baeyens, J., (**2010**).
Petrochemicals recovery through polyethylene (PE) pyrolysis: Maximizing product yields via isothermal and dynamic kinetics, In: Proc Energy from Biomass and Waste UK (EBW UK) Conference and Exhibition,
London (*England*), UK, 26th-27th January.

7. Al-Salem, S.M. and Lettieri, P. (**2010**).
Isothermal pyrolysis of various virgin and recyclate grades of polyethylene (PE) under moderate/high temperatures: Back to petrochemicals via reaction kinetics and modelling, In: Proc 6th World Congress on Particle Technology (6th WCPT),
Nuremberg, Germany, 26th-29th April.

8. Al-Salem, S.M. and Lettieri, P. (**2010**).
Kinetics of polyethylene terephthalate (PET) and polystyrene (PS) dynamic pyrolysis, In: Proc International Conference on Energy, Environment and Sustainable Development, Paper ID# 231, pp. 1496-1504, ISSN: 2070-3740
Paris, France, 28th-30th June.

Presentations:

- Presentation title: Recycling & Energy recovery routes from Plastic Solid Waste (PSW). Presented at **University College London** to HRH the Princess Royal, Anne Elizabeth, 12th Jan **2010**. MBE facility opening ceremony.

- Presentation title: Recycling & Energy recovery routes from Plastic Solid Waste.
  Presented at **University College London**, 24th June **2010**. Institution of Chemical Engineers (IChemE) seminar, *Powders: a Key Component of Sustainable Processes*.